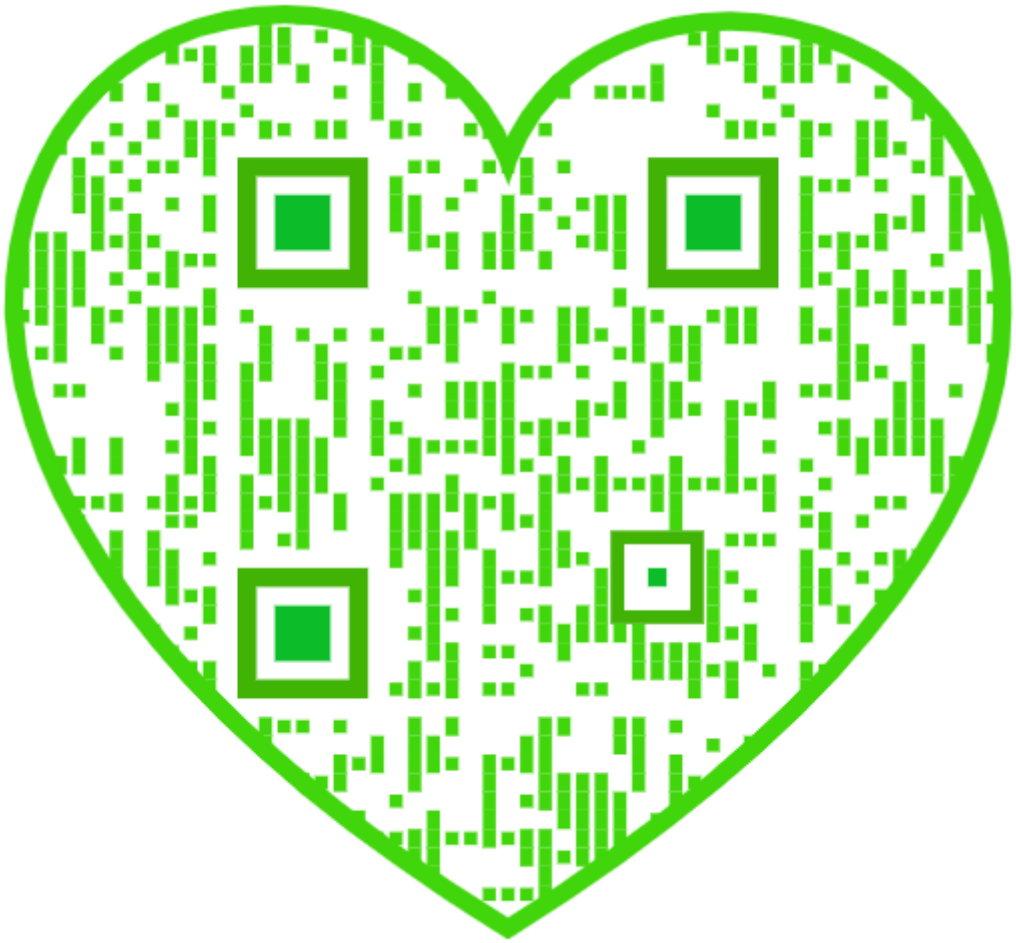

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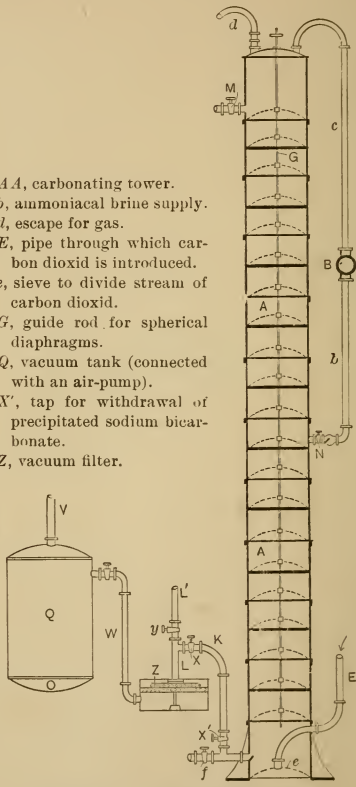

AA, carbonating tower.
b, ammoniacal brine supply.
d, escape for gas.
E, pipe through which carbon dioxid is introduced.
e, sieve to divide stream of carbon dioxid.
G, guide rod for spherical diaphragms.
Q, vacuum tank (connected with an air-pump).
X', tap for withdrawal of precipitated sodium bicarbonate.
Z, vacuum filter.

THE SOLVAY CARBONATING TOWER.

ELEMENTARY CHEMISTRY

FOR HIGH SCHOOLS AND ACADEMIES

BY

ALBERT L. AREY, C.E.

ROCHESTER (N.Y.) HIGH SCHOOL

New York

THE MACMILLAN COMPANY

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PREFACE

The course in elementary chemistry herewith presented has been in use in the author's laboratories for the past six years, and is the result of an effort to increase the usefulness of chemistry as a disciplinary subject.

The author was long since convinced that the most valuable part of the work in chemistry, from an educational standpoint, was derived from the processes of thought which the student followed when questioned by the teacher during his experiment; and the impossiblity of questioning each student in a large class individually and thoroughly led to the adoption of the plan of adding to the questions designed to guide the student's *observations* which ordinarily accompany the directions for experiments, a set of questions designed to guide the student's *inferences* and to suggest a definite line of thought in each experiment. This plan necessitated the use of the text-book as a laboratory manual, to which so many teachers object because of the marked resemblance between the notes taken by some students and the statements of the same facts in the text-book. Under these conditions it was decided to omit all reference to those properties of the substances studied in the laboratory which can be learned by observation of the substances themselves; but to render the work more complete than it would otherwise be by stating such properties as cannot be shown by experiments adapted to secondary schools.

The laboratory thus becomes a study in which the student prepares his lesson for the next day by preparing the sub-

stance assigned and studying its properties, taking complete notes as his work proceeds and writing the answers to all questions in his note book. The next day's recitation shows the character of the student's observations and of his process of thought; at this time he should be expected to give a complete account of the substance studied, including his personal observations and inferences; and the facts stated in the text-book concerning its occurrence, preparation, properties, and uses.

The syllabus in chemistry, of the New York State Board of Regents, has been used as a guide in the selection of topics for discussion and the order of their arrangement, and many of the review questions were taken from the Regents' examination papers.

In conclusion, I wish to express especial obligation for many valuable suggestions to Mr. George M. Turner of the Masten Park High School, Buffalo, who has read the entire proof.

A. L. A.

ROCHESTER, N.Y.,
November, 1899.

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SUGGESTIONS TO THE STUDENT

The subject which you are now beginning differs from those which you have pursued heretofore in several important particulars, and the benefit which you will derive from your study will depend, to a large extent, upon your ability to adapt yourself to new conditions and requirements. Heretofore you have studied statements about things, now you are to study the things themselves; and this change affords an opportunity to cultivate your observation. Let me urge you to endeavor to see all that there is to see, and to be careful that you do not think you see what has no existence.

Heretofore you have depended chiefly upon the author's judgment for inferences from facts stated, now you are to depend upon your own judgment for inferences from facts observed; and this change gives to chemistry its chief educational value. Let me urge you to assume a judicial attitude, to carefully consider all evidence, that your inferences may be fully warranted; and to see that your notes state only the truth.

The training of hand and mind which may be acquired in the manipulation of chemical apparatus is also of great value, but you must guard against the formation of habits of slovenly experimentation. It may sometimes be easier to use a piece of apparatus which is "good enough," but the satisfaction and the training acquired in arranging the perfect apparatus will more than compensate for the extra work required.

APPARATUS

Each student should be provided with the following apparatus: —

1 Bunsen burner and tube.
1 retort stand.
1 pneumatic trough (1).
1 16-oz., wide-mouth, packing bottle.
2 8-oz., wide-mouth, packing bottles.
1 two-holed rubber stopper to fit above bottles.
1 test bottle (2).
4 pieces of window glass, 2 inches square.
1 piece of wire gauze, 5 inches square.
1 piece fine copper gauze, $2\frac{1}{2}$ inches square.
1 $\frac{1}{2}$-inch deflagrating spoon.
1 test-tube brush.
1 brush for small tubing.
1 pair crucible tongs.
1 funnel, 3 inches in diameter.
1 test tube, $\frac{5}{8} \times 6$ inches.
1 ignition tube, $\frac{5}{8} \times 8$ inches (3).
1 250 cc. flask.
1 rubber stopper to fit flask and ignition tube (4).
1 evaporating dish, 3 inches in diameter.
1 flower pot saucer, 4 inches in diameter (5).
2 pieces rubber tubing, 4 inches long, $\frac{1}{8}$ hole.
2 pieces rubber tubing, 4 inches long, $\frac{1}{4}$ hole.
1 piece $\frac{1}{4}$-inch glass tubing, 9 inches long.
1 piece $\frac{1}{4}$-inch glass tubing, 13 inches long.
2 pieces $\frac{1}{4}$-inch glass tubing, 9 inches long, with 90° bend 3 inches from one end.

(1) A 4-quart tin pan, or a stoneware milk pan, will answer very well for this purpose.

(2) A 1-ounce morphine bottle, used to test the purity of hydrogen and for various other purposes.

(3) In a number of experiments the 6-inch test tube may be used instead of the ignition tube with advantage.

(4) Short pieces of the several sizes of thick-walled rubber tubing, known to the trade as shaft coupling tube, make satisfactory stoppers for flasks and ignition tubes. If too small, they may be enlarged by slipping over them pieces of larger thin-walled tubing.

(5) This serves as a support for bottles in the pneumatic trough. Any potter will make them with a $\frac{5}{8}$ hole in the centre and a triangular piece cut out of the side.

PART I

CHAPTER I

CHEMICAL ACTION

1. Elements and Compounds. — The different kinds of matter known to man may be divided into two classes:

(1) *Compounds*, or those which may be decomposed or separated into other substances.

(2) *Elements*, or those which have thus far resisted all attempts to decompose them.

About seventy simple substances or elements have been discovered, and, so far as is at present known, all compounds are the result of the chemical union of two or more of these.

It is possible that, as our knowledge of chemistry increases, many, if not all, of the substances now classed as elements may be shown to be compounds. Water was considered an element until 1783, and several other so-called elements have been resolved into simpler forms since that time.

There are many chemists who consider the seventy elements as so many unsolved problems.

2. Molecules and Atoms. — The accepted theory of the constitution of matter maintains: —

1. That it is made up of minute particles called molecules (little masses), each one of which, in a given substance, is exactly like its neighbors in *weight*, *volume*, and *structure*.

2. That they move about each other, under the influence of heat, as separate bodies.

3. That they are the limit beyond which it is impossible to subdivide matter without destroying its identity.

In accordance with this theory, each molecule of a compound is believed to contain the same elements that chemical analysis shows the large masses of the substance to contain, and these smaller portions of the elements are called atoms. There is good reason for believing that atoms rarely exist in a free state, but that the molecules of most elements consist of two or more atoms.

A molecule is the smallest particle of a substance which can exist in the free state, and which has the same composition as any larger mass of the same substance.

An atom is the smallest particle of an element that exists in any molecule.

We may now state the following definitions: —

A compound is a substance whose molecule contains two or more kinds of atoms.

An element is a substance whose molecule contains only one kind of atoms.

3. The Domain of Chemistry. — *Chemistry is that branch of science which deals with changes in the identity of substances; and with the laws, causes, and effects of such changes.*

The subject is closely related to physics; every chemical change is accompanied by some physical change, but the chemical change differs in one important particular from a physical change: the chemical change is due to forces acting upon atoms, while the physical change depends upon forces acting upon the molecule.

A physical change is one which does not destroy the identity of the substance acted upon.

Illustration. When a bar of steel is magnetized it acquires a new property, but it remains the same substance, and the change is physical.

A chemical change is one which destroys the identity of the substance acted upon.

Illustration. When a bar of steel rusts a portion of the steel is converted into a new substance which differs from the steel in color, tenacity, elasticity, and other properties.

4. Chemical Action. — In some instances one may be in doubt as to whether a chemical change has taken place, and in a few instances chemical analysis is necessary to prove it. But in general the occurrence of any of the following phenomena, when two or more substances are mixed, may be taken as evidence of chemical action: —

1. Effervescence.
2. The evolution of heat and light.
3. Change of color.
4. Change of volume.
5. Change of state.
6. The development of electricity.

Exceptions. 1. A change of state by solution of a solid or gas.

2. A change of volume due to the absorption of a gas by a solid or liquid, or to a change in temperature.

Take notes on the following experiments which will be performed by the instructor, and designate them as physical or chemical changes: —

Experiment I. — Sugar and potassium chlorate are mixed, and a drop of sulfuric acid added.

Experiment II. — Sulfuric acid is added to syrup.

Experiment III. — A rubber ruler is electrified.

Experiment IV. — A beam of sunlight is decomposed with a prism.

Experiment V. — A piece of platinum wire is heated to redness.

Experiment VI. — A piece of magnesium wire is heated to redness.

Experiment VII. — Sulfur and potassium chlorate are mixed in a mortar with considerable friction.

Experiment VIII. — Solutions of potassium iodid and mercuric chlorid are mixed.

Experiment 9 and the succeeding experiments are to be performed by the pupil unless special directions to the contrary are given.

Experiment IX. A Chemical Change. — 1. Examine a piece of marble carefully, fix its appearance in mind, so that you can detect any change.

2. Drop a small piece in the test bottle and cover it with dilute hydrochloric acid. What occurs?

3. After a short time test the gas in the upper part of the test bottle with a lighted match. Does the match continue to burn? Is the gas combustible? Is the gas ordinary air? Why? Does the marble disappear?

4. In order to tell whether the marble has been changed chemically, the acid must be expelled. To accomplish this, pour the solution into an evaporating dish, place it on a piece of wire gauze, and bring the liquid to a boil. When the liquid begins to solidify and turn yellow, add a few drops of water, repeating, if necessary, to obtain a solid white residue.

Examine this residue, compare it carefully with marble. Set the residue aside for 24 hours to determine whether it is permanent when exposed to the air.

Fill out the following table: —

	Marble	Residue
Is it hard or soft?		
Does it effervesce with hydrochloric acid?		
Is it soluble in water?		
Is it permanent in air?		

How do the properties of the residue compare with those of marble?

Is it marble?

What have you proven?

Experiment X. — Bring together on a flower-pot saucer a little phosphorus and iodin. What evidence have you that chemical action took place? Have either of the original substances disappeared? Has a new substance been formed? It will be seen that simple contact is sufficient to cause the two substances to act upon each other.

Does either substance melt? Why?

Is this a case of chemical action between solids?

Is the action as energetic at first as it is after a few seconds? Explain.

CAUTION. — Handle phosphorus with great care; it takes fire when rubbed or cut in the air, and should always be kept in water.

5. Conservation of Matter.

Experiment XI. — Pour 10 cc. of dilute sulfuric acid into a beaker. In a second beaker pour an equal quantity of calcium chlorid solution. Place both beakers in one scale pan and balance them carefully with weights, sand, or shot, placed in the other scale pan. Now pour the calcium chlorid into the sulfuric acid. Does a chemical change occur? Replace the beakers and determine whether the weight of the beakers and their contents has been changed. Does chemical action change the total quantity of matter in existence? Was the total quantity of sulfuric acid in the world increased or diminished by the above experiment? How was the total quantity of calcium chlorid affected? of the white substance formed?

6. The Effect of Solution on Chemical Action.

Experiment XII. — Place as much baking soda as you can take on the end of a knife blade in a dry test bottle. Add an equal amount of tartaric acid; shake the bottle to mix the powders thoroughly. Has any change occurred?

Pour a few cubic centimetres of water into the bottle. What evidence of chemical action do you observe?

Does solution aid chemical action? Is it because more intimate contact of the molecules is obtained when solutions are mixed than is possible with solids? Should diminishing cohesion assist chemical action? State your opinion as to why solution aids chemical action.

7. Effect of Heat on Chemical Action.

Experiment XIII. — 1. Mix six grammes of potassium chlorate and one gramme of powdered charcoal thoroughly. What occurs?

2. Apply a lighted match. Was the change chemical or physical?

How does the operation of striking a match illustrate the effect of heat upon chemical action?

Why do metals rust more rapidly when hot than at lower temperatures? Experiment 22 illustrates this effect. Do fuels combine with the air when cold?

8. Light causes Chemical Action.

Experiment XIV. — Cut a design from tin-foil and place it on a piece of blue print paper. Expose paper and design to sunlight for a few minutes. Wash the paper in water.

Has the sunlight affected the exposed chemical? In what way?

The art of photography is based on the action of light on chemicals. In growing plants sunlight causes the decomposition of carbon dioxid, which is only accomplished by the chemist with difficulty.

In the preparation of hydrochloric acid by synthesis described on page 93, the chemical action is assisted by light.

QUERY. — Why do certain colors fade when exposed to light?

9. Pressure. — When the two gases, hydrochloric acid and hydrogen phosphid, are subjected to increasing pressure they combine to form a crystalline solid known as phosphonium chlorid. Similarly sulfur and powdered lead may be caused to combine by great pressure, forming lead sulfid.

QUERY. — What relation does this action suggest between the intensities of chemical affinity and distances between molecules?

10. Concussion or Detonation. — In a very few cases, chemical action is brought about by detonation. The molecules of the gas acetylene consist of two atoms of carbon united with two of hydrogen. If a small quantity of mercury fulminate be detonated near a globe filled with this gas the carbon is instantly deposited in solid form and the hydrogen liberated. This action is not fully understood; some chemists believe that the particular form of sound vibration produced disturbs the motions of the atoms constituting the molecule, and thus causes disruption.

11. Electricity. — If a current of electricity be passed through a solution of copper sulfate, the compound is de-

composed, and many other compounds are affected in the same way. In Experiment 40 this effect is also illustrated.

12. The Effect of Trituration on Chemical Action.

Experiment XV. — Using pincers, hold a small lump of rosin in the Bunsen burner flame, observe the character of the flame produced by the burning rosin. Is rosin easily ignited? Does it burn rapidly? Does the rosin melt before it ignites?

Experiment XVI. — Triturate a small piece of rosin in a mortar, fill the end of a large glass tube with the powder and blow it into the burner flame. Does the finely divided rosin burn with a smoky flame or does it flash? Does it burn as rapidly as in the previous experiment? How does the energy of the chemical action compare with that observed in the last experiment? In which case is the higher temperature reached?

Experiment XVII. — Make a compact pile of about $\frac{1}{2}$ cu. cm. of powdered rosin on a piece of porcelain or earthenware, ignite with a Bunsen burner. How does the chemical action compare with that of the previous experiment? Does the increased chemical action depend upon the size of the particles? Would a solid piece having the same area as the sum of the surfaces flash? Does the chemical activity depend upon the surface only? Upon the mass of the particles only?

13. Mechanical Mixture.

Experiment XVIII. — 1. Mix about four grammes of sulfur and an equal weight of fine wrought iron filings on a sheet of paper. Divide into three portions.

2. Examine the first portion with a magnifying glass. Can you distinguish the particles of sulfur from those of iron? Can you separate the iron from the sulfur with a magnet? Now put the mixture in a test tube and pour water on it. Are the substances combined or not? Shake the tube; what is the yellow substance floating on the water? Has chemical action taken place?

3. Treat the second portion with carbon disulfid. What is the black substance at the bottom of the tube? What has happened? Is the color of the carbon disulfid changed? What does this indicate? Is a chemical compound formed in this experiment?

Experiment XIX. — 1. Put the third portion of the mixture made in Experiment 18, in a dry test tube and heat gently. When it is red hot remove the tube from the flame. Is there any evidence of combustion in the tube?

2. After the action is over and the tube has cooled down, loosen the contents with a short piece of wire, and pour it out on a piece of paper. Does the mass look like the mixture of sulfur and iron with which you started?

3. Examine with a magnifying glass. Can you separate the sulfur and iron with water as before? Can you separate them with a magnet?

4. Treat a portion of the mass with carbon disulfid. Is the effect the same as before? Is the color of the carbon disulfid changed? What do you conclude concerning the effect of heat on the mixture?

REVIEW QUESTIONS

1. Define chemical action. What assists it? What retards it?

2. Mention those conditions which aid chemical action, (*a*) by decreasing the distance between the unlike molecules, (*b*) by diminishing the cohesion of the factors.

3. Describe an experiment to show that there is no loss of matter in chemical change.

4. Distinguish between a mechanical mixture and a chemical compound. Illustrate each.

5. Distinguish between chemistry and physics; between atoms and molecules; between chemical changes and physical changes.

6. What mechanical mixture was formed in Experiment 12? In what part of the experiment were chemical compounds formed?

Write answers to these questions in your note-book.

CHAPTER II

SYMBOLS AND LAWS

14. Symbols. — Chemists of all countries have agreed to use the initial letter of the Latin name of an element as an abbreviation which shall stand for a single atom of that element. In case two or more elements begin with the same letter the second characteristic letter is added to the symbol, thus: —

C	Carbon	N	Nitrogen	Na*	Sodium
Ca	Calcium	S	Sulfur	K*	Potassium
Cl	Chlorin	Si	Silicon	Ag	Silver

Some writers use these symbols as mere shorthand signs for the full names of the elements. This usage is extremely objectionable; students who adopt it will not appreciate the important quantitative relations which are shown by reactions.

15. Formulæ. — Compounds are represented by a formula or a group of symbols, showing the composition of the molecule of the substance.

Thus, the formula of sodium chlorid, NaCl, indicates that its molecule contains one atom of sodium and one of chlorin, and CaS represents a molecule of calcium sulfid which contains one atom of calcium and one of sulfur.

If a molecule contains more than one atom of a given

* The Latin name of sodium is *Natrium*, that of potassium is *Kalium*.

element, a subnumber is placed a little below and to the right of the symbol, and indicates the number of such atoms. Thus $CaCl_2$ is the formula for calcium chlorid, which contains one atom of calcium and two of chlorin, and the formula for ferric oxid, Fe_2O_3, tells us that its molecule contains two atoms of iron and three of oxygen.

If more than one molecule of the substance is to be represented, the number is placed before the group of symbols. Thus $2\,Fe_2O_3$ represents two molecules of ferric oxid containing four atoms of iron and six of oxygen.

In the absence of a coefficient a formula always represents a single molecule.

16. The Law of Constant Proportions. — The law of definite proportions which has been called the corner stone of modern chemistry is as follows: —

"The same compound always contains the same elements combined in the same fixed and definite proportions."

The thousands of analyses which have been made of various compounds by chemists in all parts of the world, and which are now being made every day, are based upon this law, and in no single instance have the results obtained caused the truth of the law to be questioned.

17. Combining Weights. — Another important relation is to be learned from a study of the composition of various substances. Not only is the proportion by weight in which a certain element combines with a certain other element, to form a given compound, constant, but it is possible to select a number for each element, which shall represent the proportion by weight in which it unites with different elements.

The composition of the oxids mentioned thus far is given below: —

Mercury, 200	Lead, 207	Iron, 56
Oxygen, 16	Oxygen, 16	Oxygen, 16
Copper, 63.6	Zinc, 65.4	
Oxygen, 16	Oxygen, 16	

In each of the above compounds it is observed that there are 16 parts by weight of oxygen, and this number or a simple multiple of it will express the proportion in which oxygen combines with any other element.

Such numbers have been carefully determined for all elements and are called combining weights.

18. The Law of Multiple Proportions. — The analysis of various substances further shows that a given element may combine with another in more than one proportion. For example, the elements nitrogen and oxygen form several compounds having the following composition: —

	Nitrogen	Oxygen
Nitrous oxid	28 parts	16 parts
Nitric oxid	28 parts	32 parts
Nitrous anhydrid	28 parts	48 parts
Nitrogen peroxid	28 parts	64 parts
Nitric anhydrid	28 parts	80 parts

It will be observed that while the quantity of nitrogen is the same in all the above compounds the quantity of oxygen varies, being twice as great in the second compound as in the first, three times as great in the third as in the first, etc. This series illustrates the law which applies to all cases in which more than one compound is formed from the same elements.

If two elements form more than one compound, the proportions by weight in which a given element combines with the other in each compound will be expressed either by its combining number or a simple multiple of its combining number.

19. The Atomic Theory. — The atomic theory was suggested by John Dalton, an English schoolmaster, early in this century, to account for the laws of definite and multiple proportions. It maintains —

1. That with a few possible exceptions all molecules are made up of smaller particles.

2. That these particles are indivisible (they are therefore called atoms).

3. That all atoms of a given element are equal in size and weight.

4. That atoms of different substances have different weights.

5. That the combining weights of the elements are simply the relative weights of the atoms, and may therefore be called the atomic weights.

The explanation of the facts of chemistry which this theory offers is so satisfactory that it is universally accepted.

20. Atomic Weights. — As hydrogen enters into combination in smaller proportion than any other element, its combining weight or atomic weight is taken as the unit. When we say that the atomic weight of oxygen is 16, we mean simply that the atoms of oxygen are sixteen times heavier than those of hydrogen. The exact weight of an atom of hydrogen has never been determined but it is called a *microcrith*. The atom of oxygen weighs 16 microcriths.

The following table gives the exact values of the atomic weights of the elements referred to in this book. The standard is Oxygen = 16.

TABLE OF ATOMIC WEIGHTS

Name	Sym.	O = 16	Name	Sym.	O = 16
Aluminum	Al	27.11	Antimony	Sb	120.42
Argon	A	(?)	Arsenic	As	75.01
Barium	Ba	137.43	Bismuth	Bi	208.11
Boron	B	10.95	Bromin	Br	79.95
Cadmium	Cd	111.95	Calcium	Ca	40.07
Carbon	C	12.01	Chromium	Cr	52.14
Chlorin	Cl	35.45	Copper	Cu	63.60
Cobalt	Co	58.93	Gold	Au	197.23
Fluorin	F	19.06	Iodin	I	126.85
Hydrogen	H	1.008	Lead	Pb	206.92
Iron	Fe	56.02	Magnesium	Mg	24.28
Lithium	Li	7.03	Mercury	Hg	200.00
Manganese	Mn	54.99	Nitrogen	N	14.04
Nickel	Ni	58.69	Phosphorus	P	31.02
Oxygen	O	16.00	Potassium	K	39.11
Platinum	Pt	194.89	Silver	Ag	107.92
Silicon	Si	28.40	Strontium	Sr	87.61
Sodium	Na	23.05	Tin	Sn	119.0
Sulfur	S	32.0	Zinc	Zn	65.41

21. Reaction. — The force which is exerted between atoms is called *chemical affinity*. The affinity of a given atom for other atoms varies greatly, often being very strong for certain kinds of atoms and feeble for others. If, when any substances are mixed, a rearrangement of the atoms would produce more stable compounds, *i.e.* if the force which holds the atoms together in the new compounds is stronger than that which bound them in their original form, such rearrangement will take place. The process of redistribution of the atoms in the molecules concerned in the phenomenon is called *chemical action* or *reaction*.

A reaction is due to chemical affinity and causes a chemical change.

Substances used to bring about desired reactions are called *reagents.*

The substances which go into a reaction are called *factors,* and those which come from a reaction *products.*

Reactions are ordinarily expressed by *equations* in which the symbols and formulæ of the factors are placed on the left of the sign of equality, and those of the products on the right. The algebraic signs plus and minus are used in the ordinary sense in the equations.

The fact that atoms can neither be created nor destroyed, even by chemical means, justifies the use of the sign of equality to connect factors and products, and it should never be placed until the student has "satisfied the reaction," *i.e.* has determined that there are exactly as many atoms of each element in the products as there are in the factors.

Illustration. In Experiment 11 the following reaction occurred: —

$$CaCl_2 + H_2SO_4 = CaSO_4 + 2\,HCl.$$

This should be read as follows: one molecule of calcium chlorid plus one molecule of sulfuric acid forms one molecule of calcium sulfate plus two molecules of hydrochloric acid.

The chemical change occurring in Experiment 19 may be expressed as follows: —

$$Fe + S = FeS.$$

Such equations express very concisely the relations between the atoms and molecules in the chemical changes which they represent, and every chemical change which is clearly understood may be expressed in this way. Equations are also useful because of the important quantitative relations between masses which are made evident when we consider the atomic weights of the elements represented.

In the equation given above, the symbol Fe not only signifies an atom of iron, but it also stands for 56 parts of iron, by weight, and the symbol S stands for 32 parts of sulfur by weight. We thus have a mathematical expression which shows the relation between the masses of iron and sulfur which take part in the chemical change.

$$\begin{array}{ccccc} \mathrm{Fe} & + & \mathrm{S} & = & \mathrm{FeS} \\ 56 & & 32 & & 88 \end{array}$$

The equation can now be read: —

56 parts of iron unite with 32 parts of sulfur to form 88 parts of ferrous sulfid. The solution of many chemical problems depends upon this use of equations. (See Chapter IX.)

22. Analysis, Synthesis, and Metathesis. — All chemical changes may be referred to one of four classes: —

(*a*) Compound molecules may be separated into their elements, or into simpler groups of elements, as, for example, mercury rust is separated into mercury and oxygen in Experiment 25, or as potassium chlorate $KClO_3$, is decomposed in Experiment 30, forming potassium chlorid KCl, and oxygen. Such changes are analytic, and the process which brings them about is known as *analysis*.

(*b*) Compound molecules may be formed by direct union of elements, or simpler groups of elements, as when phosphorus combined with iodin, in Experiment 10, forming phosphorous di-iodid PI_2, or when carbon monoxid CO, combines with oxygen to form carbon dioxid CO_2. (See Experiment 101.) Such changes are synthetic, and the process is known as *synthesis*.

(*c*) Compound molecules may be formed by a change involving both analysis and synthesis, which is known as *metathesis*, or double decomposition. In such processes an exchange of atoms, or groups of atoms, takes place between two compound molecules, as when a solution of sodium sulfate Na_2SO_4, and barium chlorid $BaCl_2$, are mixed. Each substance is decomposed, and the atoms combine to form two new substances, barium sulfate $BaSO_4$, and sodium chlorid NaCl.

(*d*) In some cases new substances are formed without changing either the kinds of atoms, or the number of atoms of each kind, in the molecule. For example, when a solution of ammonium cyanate $NH_4 . O . CN$, is heated it is transformed into urea N_2H_4CO, a substance having entirely different chemical and physical properties. It will be observed that these molecules contain the same number of atoms of each element; we have excellent evidence, however, that the first one contains cyanogen CN, while the second contains carbon monoxid CO.

REVIEW QUESTIONS

1. How many atoms of hydrogen in $6\,H_2SO_4$? of sulfur? of oxygen?

2. How many atoms of each element are represented by the following formulæ: $2\,ZnCl_2$, $3\,HNO_3$, $5\,H_2O$, $14\,NH_3$.

3. How many molecules of each substance are represented by above formulæ?

4. Define chemical affinity, reaction, reagent, factor, product.

5. Distinguish between atoms and molecules. Does a chemical affinity exist between molecules? Give a reason for your answer.

6. What is atomic weight? How is atomic weight related to specific gravity?

7. What element is selected as the standard of atomic weight? Why is this element selected?

8. State the atomic theory.

9. State five principles observed in writing chemical symbols and formulae.

10. What is a chemical equation? What is meant by the combining weight of an element?

11. State the law of constant proportions. Of multiple proportions.

12. State five principles to be observed in writing chemical equations.

CHAPTER III

CHEMISTRY OF THE AIR

23. The Formation of Rust.

Experiment XX. — 1. In a small porcelain crucible or a clay pipe bowl put a small piece of lead or zinc. Heat with laboratory burner and notice the changes that take place. Do not allow the containing vessel to become too hot, for liquefied rust will be absorbed. After the lead begins to melt, stir with a thick iron wire. Observe carefully what forms on the surface of the metal. Does the lead retain its bright mirror-like surface if not stirred? Continue to heat and stir until the substance is changed to a powder. What is its appearance now?

2. Let it cool. Is it lead? What difference is there between the action in this case and in melting ice and cooling the water again? Which is chemical and which is physical action? Why? Was the change just observed produced by the heat or by the action of the air? In order to answer this question let us repeat the experiment, preventing any action of the air by covering the metal with a film of melted rosin.

Experiment XXI. — Repeat Experiment 20, adding as much powdered rosin as can be lifted on the blade of a penknife. Do not stir the metal. Does it rust or does the surface remain bright and mirror-like? Is it changed to powder? How do you explain the difference in result of this experiment and the last? What do you conclude concerning the cause of the change produced in the previous experiment? Is the action due to the high temperature or to the action of the air or to both? Does lead rust more rapidly at high than at low temperature? Rosin is used to prevent rusting of hot metals in process of soldering.

24. Effects of Air on Iron at Ordinary and at High Temperatures.

Experiment XXII. — Wind a piece of No. 30 iron wire about a foot long around the finger and heat the loops thus formed in the tip of a laboratory burner flame for a minute or two. Holding the loop over a sheet of paper, straighten the wire. Compare the scale which drops

off with the rust formed on iron at ordinary temperatures. Is it the same color? Does iron rust more rapidly at high or low temperatures? How do you know? Has a chemical change occurred? Pass a magnet over a mass of red rust; of black rust. Are they magnetic? (See paragraph on Oxids in Nature, page 37.)

25. Various Ways of Protecting Iron.

Several years ago Professor Barff, of London, suggested that iron might be protected from the action of the air by exposing it to superheated steam at high temperature, thus forming a coating of black rust on its surface. The process has been somewhat modified, and is now known as the Bower-Barff process. It is quite extensively employed as a finish for iron ornaments, and has been used in certain cities to protect water pipes.

Zinc and lead are protected from the action of the air by the coating of oxid which forms on their surface.

Queries. — Mention several ways of protecting iron from the action of the air. Why do we blacken stoves? Why are some parts nickel plated? What is galvanized iron? What is a tin pan made of? In what two ways are water pipes protected? How are iron bridges protected? Bicycle frames?

26. Does the Weight of a Metal change when it rusts?

When a chemical change occurs it is due to the addition of some element or elements to the substance changed, or to the extraction of some element or elements from the substance changed. Now, since loss or gain in matter means loss or gain in weight, let us determine whether a substance was added to or driven off from the iron in the last experiment.

Experiment XXIII. (Performed by the instructor.) — Weigh a piece of No. 30 wire, heat as in the last experiment; when cool weigh again. Explain.

Does heating in contact with air drive something away from the iron or cause something to combine with it? From what source is the substance derived?

27. The Material which combines with the Metal to form Rust.

We now desire to know the nature of the substance which causes metals to rust; and as it can be expelled easily from the rust which forms on mercury, we shall study that substance. As air is an invisible gas, special precautions must be taken to prevent its loss or mixture with other substances.

Experiment XXIV. A Method of Collecting Gases. — Fill the yellow dish (see description of apparatus, p. xi) one-third full of water. Place the flower-pot saucer bottom side up in the water. Fill one of the medium sized bottles with water, cover with a glass plate, and invert on the flower-pot saucer; remove the glass plate. If your work has been carefully performed your bottle will be full of water. (If not, try again.)

Now put the end of a glass tube at the opening at the side of the flower-pot saucer and blow gently through it. What do you notice? What is in the bottle after the water is out of it? Where does it come from?

This method of collecting gases over water may be used for all gases not dissolved by water.

Students should attempt to devise other methods. Could a rubber bag be used? What advantage has the method used in this experiment over other methods?

Experiment XXV. A Study of Mercury Rust. — 1. Weigh accurately a small glass tube, closed at one end, containing about a gramme of mercury rust.

2. Holding the tube in a nearly horizontal position with a pair of crucible tongs, heat the red powder strongly for some minutes, or until a bright mirror-like deposit appears near the open end of the tube.

3. Weigh the tube again. Is there any evidence that an invisible substance has escaped? After weighing the tube, examine the deposit near the open end. Scrape some of it from the tube with an iron wire; what is it? What have you learned about the constituents of mercury rust? Is either constituent a solid? a liquid? a gas?

4. Arrange an ignition tube, as shown in Fig. 1, so that any gas generated in the tube may be collected in the bottle. Fill the bottle with water.

5. Put about 15 grammes of mercury rust in the ignition tube and apply heat. Describe the gas collected.

6. Test with a glowing match stick. Remove the match and put it back a few times. Is there any difference between the burning in the bottle and out of it? Is the gas air? Has the gas which formed the rust a marked ability to make things burn? Has the color of the mercury rust changed?

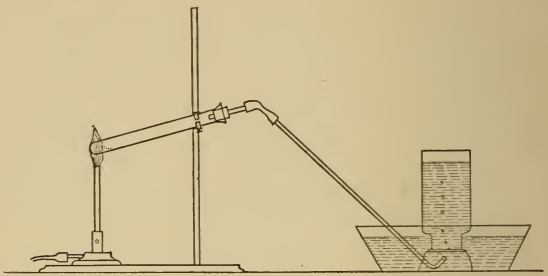


Fig. 1.

7. Remove the ignition tube and pour its contents on a piece of paper. How is the color affected? Compare it with some of the mercury rust which has not been heated. What effect has the air had upon the hot rust from the tube? Has the air entirely restored the gas driven off by the heat? Is the gas collected in this experiment pure air, or a part of the air?

The chemical change which occurs in this experiment may be expressed as follows: — $HgO = Hg + O$.

The gas which causes metals to rust is called *oxygen*, its compounds are called *oxids*, and the process of forming oxids is known as *oxidation*. The rust formed on iron at ordinary temperatures is called ferric hydroxid. That formed at high temperatures is ferrous oxid and ferric oxid, probably in chemical combination. It is called magnetic oxid.

We have observed that oxygen makes things burn vigorously, and, although it is deemed best to reserve the discussion of combustion for a subsequent chapter, the next two experiments are given here to show the relation between the processes of rusting and burning.

28. Effect of excluding the Air from a Flame.

Experiment XXVI. — Close the holes at the bottom of your laboratory burner. How is the character of the flame affected? Explain. Why do we close the stove dampers at night? What is the effect of removing the ashes and clinker from a stove? Why?

Suggestion. — Wrap a piece of cloth around the lower part of a kerosene lamp burner, covering the holes through which the air enters the chimney. How does this affect the flame? What has air to do with the combustion of oil? How does a lamp chimney increase the brightness of the lamp flame? How does a fire extinguisher put out a fire? It is possible that burning, like rusting, is simply a chemical union of air, or a part of the air, with the fuel. Let us determine whether this is so by the method used in Experiment 23.

29. Comparison of the Weight of the Products of a Burning Candle with the Amount lost by the Candle.

Experiment XXVII. (Performed by the instructor.)— On one side of a delicate balance, apparatus which will absorb the products of combustion is suspended over a candle, the whole being exactly balanced with weights on the other side of the balance. The candle is lighted and the gases are drawn into the absorbing apparatus. As the candle burns away the side of the balance carrying the apparatus grows heavier. The weight of the products is greater than the loss of weight of the candle.

Is the candle converted into heat? Is heat matter? Where does the matter causing the increase come from? Does this prove that the candle is indestructible? What is your conclusion concerning the nature of combustion?

30. Analysis of the Air. — We have learned that oxygen is a part of the air, and now desire to learn what proportion of the air is oxygen.

Experiment XXVIII. To determine the per cent of oxygen in the air. Cooley's method. Apparatus required. — A small glass funnel. A six-inch test tube, with a two-holed rubber stopper to fit same. Rubber bands, a measuring glass, 155 cc. of the absorbent liquid. A piece of glass tubing two inches long fitted in one of the holes of the stopper, a piece of glass rod the same length in the other hole, and a piece of thin rubber tubing six inches long, in which a piece of glass

rod half an inch long and of such size as to prevent a liquid from running through the tube, is placed.

Manipulation. — 1. Arrange the apparatus as shown in Fig. 2.

2. In your test bottle dissolve a small teaspoonful of pyrogallic acid in 10 cc. of water, quickly add 5 cc. of a strong solution of sodium hydroxid, and pour into the funnel. This liquid absorbs oxygen and carbon dioxid rapidly.

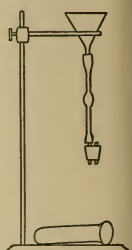


Fig. 2.

3. Holding the test bottle under the rubber cork, pinch the rubber tube where the glass rod closes it until a little of the liquid runs through the tube. Carefully remove the drop which is suspended from the glass tube with a piece of filter paper.

4. Now remove the glass rod from the hole in the rubber stopper and put the test tube on the stopper; allow it to hang there a minute or two to allow the heat communicated to the tube and air which it contains to pass away. Then insert the glass rod in the open hole in the stopper. We have now isolated a definite volume of air at the same temperature and pressure as the air of the room, and during the absorption and the measurements care must be taken to prevent change in the volume under analysis, either by the escape of a portion or by the introduction of more air from without.

5. Pinch the rubber tube at the glass rod to allow some of the absorbent liquid to run down into the test tube; a little stream runs in at first, then drops follow each other more and more slowly; when these have nearly ceased allow the apparatus to stand for two or three minutes. Then allow more of the absorbent liquid to enter the test tube. Repeat the operation every two minutes until only a drop or two enters the tube when opened.

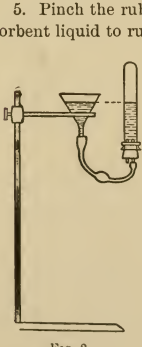


Fig. 3.

6. The gas in the test tube is now compressed by the weight of the liquid in the rubber tube; before measurements can be made the pressure must be adjusted to that of the air in the room. This is accomplished by grasping the test tube by the flange (so as not to warm the gas), raising the tube as shown in Fig. 3, and pinching the rubber tube to open a passage between the two masses of liquid. Keep this passage open and move the test tube up or down until the liquid stands at the same level in the test tube

and the funnel; then close the passage between them. Your results will depend to a great extent upon the care with which this adjustment is made.

7. Slip a rubber band around the test tube so that its upper edge marks the position of the bottom of the stopper.

8. Remove the test tube from the apparatus and pour the absorbent liquid into a measuring glass. This represents the volume of gas absorbed; record the number of cubic centimetres.

9. Now fill the test tube with water to the top of the rubber band and measure this volume. This represents the volume of air analyzed.

We have thus determined the number of cubic centimetres of oxygen in a certain number of cubic centimetres of air, from which we may determine the number of cubic centimetres of oxygen in 100 cc. of air; *i.e.* the percentage of oxygen in air.

31. Other Substances in the Air. — When a gas called carbon dioxid is passed through lime water the latter becomes cloudy because a white solid (a precipitate) is formed. This is the test for carbon dioxid.

Experiment XXIX. — 1. Take 20 or 30 cc. of lime water in your test bottle. Blow through a glass tube in such a way that the exhaled air bubbles through the lime water. Does the lime water become cloudy or does it remain clear? What does this experiment prove regarding air exhaled from the lungs?

2. Force air from a bellows through lime water. What inference do you draw from this experiment?

Carbon dioxid was absorbed with the oxygen in Experiment 28, but the amount is so small (about $\frac{1}{20}$ of one per cent) that it may be disregarded.

Does water vapor exist in the air? To answer this question, think of the moisture which collects on the outside of an ice pitcher in summer. What is dew? What is frost?

The gas which remains in the apparatus after absorbing the oxygen and carbon dioxid (Experiments 28 and 31) is nearly pure nitrogen. Nitrogen is fully discussed in Chapter VI.

ARGON

SYMBOL A. — ATOMIC WEIGHT 19.9

32. Some years ago Lord Rayleigh proved that nitrogen obtained by removing the oxygen from the air was invariably denser than that obtained from chemical compounds. He undertook to determine the cause of this difference, and in conjunction with Professor Ramsay found that this greater density was due to the presence of an unknown gas, which they succeeded in isolating and to which they gave the name Argon. Their discovery was announced January 27, 1895.

Argon is a gas forming $\frac{1}{120}$ part of the air; it is also found among the occluded* gases in some specimens of meteoric iron. As indicated by its name, argon is the most inert element; it has thus far resisted all attempts to get it to combine with other elements. Its chief characteristic, therefore, is its "glorious uselessness." It is sparingly soluble in water, boils at $-187°$ C. and freezes at $-189°$ C.

Since the discovery of argon several other new elements have been found in the air, with properties quite similar to those of argon.

33. Air as a Mixture. — Air is believed to be a mechanical mixture of nitrogen and oxygen, and not a chemical compound, for the following reasons: —

1. Air contains approximately 79 % of nitrogen and 21 % of oxygen. This is not in accordance with the law of multiple proportions.

2. If nitrogen and oxygen be mixed in the above proportions the mixture possesses all the properties of air, but is not accompanied by any phenomena which indicate chemi-

* Define term.

cal action. Whenever chemical union takes place, there is some change in the temperature of the substance; when nitrogen and oxygen are mixed as above described there is no change in the temperature.

3. The law of definite proportion states that the composition of a given chemical substance is invariable; that of air varies slightly.

4. Air is somewhat soluble in water, but each gas is dissolved independently.

If we shake up air and water in a bottle some of the air will be dissolved; if we boil this saturated water the air which escapes can be collected and analyzed. This has often been done, and it has been found to contain a larger proportion of oxygen than the original atmospheric air.

Thus	Atmospheric	Dissolved
N	79.04	66.36
O	20.96	33.64

This change in the proportion could not occur if the air was a compound, for a compound is dissolved as a whole. The above numbers exactly agree with the solubilities of oxygen and nitrogen separately.

REVIEW QUESTIONS

1. Describe the effects of the partial and of the total exclusion of air from a flame.

2. State how the effect of air on iron at high temperatures differs from the effect of air on iron at ordinary temperatures.

3. Describe a chemical method of protecting iron from the action of the air.

4. How does the weight of the products of the combustion compare with the amount lost by the candle? Why?

5. Does the weight of the scale which flies from the blacksmith's hot iron equal the weight lost by the iron? Why?

6. Has air a chemical formula?

7. Is the air a mixture or a compound? Describe an experiment to prove the correctness of your answer. Give reasons for your answer.

8. Describe the Bower-Barff process of protecting iron.

9. Give an account of the discovery of argon. State the properties of argon and its occurrence in nature.

10. Explain the effect of excluding air from a flame. Mention some practical appliance whose efficiency depends on the principle involved.

11. What is the scale which accumulates about the blacksmith's anvil?

CHAPTER IV

OXYGEN

Symbol O. — Atomic Weight 16

34. Occurrence. — Oxygen is the most abundant of all the elements, comprising by weight $\frac{1}{5}$ of the air, $\frac{8}{9}$ of the water, $\frac{3}{4}$ of all the animal bodies, and about $\frac{1}{2}$ of the crust of the earth.

The word oxygen means "acid-former," but it is a misnomer. Chemists supposed that it was present in all acids when the name was given.

35. Preparation. — Oxygen may be easily obtained by heating potassium chlorate.

Caution. — The following precautions must be observed: —

1. The chemicals must be free from impurities which might cause an explosion. If a small quantity of the mixture when heated in a dry test tube melts quietly, the mixture may be considered safe.
2. The ignition tube must be inclined.
3. It must not be more than one-third full.
4. The upper part of the mixture in the tube should be heated first.
5. The heat must be so regulated that an even and not too rapid flow of the gas may be secured. It may be necessary to withdraw the flame and replace it when the gas slackens.

Experiment XXX. (Two students will work together.) — 1. Arrange the apparatus as in Experiment 25. Mix equal weights of manganese dioxid and potassium chlorate, and heat about ten grammes of the mixture in a test tube. Collect four bottles of the gas evolved over water.

2. Place the bottles on the table, mouth upwards, covering them with a glass plate. What is the color of the gas? Odor? Taste? Is it soluble in water? The slight cloud which appears in the bottle

at first is due to a substance which is not oxygen. After a while this disappears and oxygen remains.

3. Drop a piece of charcoal, obtained by charring the end of a match stick, in the first bottle. In another lower a deflagrating spoon containing a little sulfur.

4. In the third drop a piece of phosphorus about the size of a pea. (Care!) Let them stand quietly and observe what changes, if any, take place. Does oxygen at ordinary temperatures act readily on these substances?

5. Now thrust a piece of red-hot charcoal (a glowing match stick) into the first bottle. Note difference in action.

6. Remove the deflagrating spoon from the second bottle; set fire to the sulfur. Notice whether it burns with ease or with difficulty. Does the sulfur burn more readily in the oxygen than in the air?

7. Remove the phosphorus from the third bottle; place it in the deflagrating spoon, ignite, and quickly lower it into the bottle again. Describe the action. How does the action of oxygen on these substances at high temperatures compare with the action on the same substances when cold? Does either substance burn as vigorously in air as in oxygen?

Reaction: $2\,KClO_3 + MnO_2 = 2\,KCl + MnO_2 + 3\,O_2$.

The Test for Oxygen. — Thrust a glowing splinter of wood into one of the bottles. What occurs?

NOTE. — No substance but oxygen can cause a spark to burst into flame. How can you determine whether a bottle contains oxygen or not?

36. Physical Properties. — Pure oxygen is colorless, odorless, and tasteless; it is heavier than air. What are its other physical properties? It is only sparingly soluble, water dissolving only 3% of it. Oxygen may be liquefied at −118° C. by a pressure of fifty atmospheres. The liquid has a pale steel-blue color, and boils at −181° C. under ordinary pressure.

37. Chemical Properties. — Oxygen combines with every known substance except fluorin, and is characterized by great chemical activity. It is the great supporter of com-

bustion. If both the oxygen and a combustible substance be *absolutely dry,* it has been shown that they will not combine. No satisfactory explanation of this fact has been offered. Oxygen is the only element capable of supporting respiration. Fish breathe the dissolved oxygen in water.

38. Uses. — Oxygen is necessary to animal respiration, to ordinary combustion, fermentation, and decay. It is used in the arts to increase the intensity of combustion, and is also used in medicine.

39. Burning in Air.

Experiment XXXI. — 1. Pour 10 cc. of lime water into a bottle containing air, shake the bottle, note the effect on the lime water; now, using a short piece of wire as a handle, lower a burning match into the bottle; when it has gone out cover with the hand and shake the bottle; note the changed appearance of the lime water. A milky appearance proves the presence of carbon dioxid.

2. Repeat the experiment using a bottle of oxygen.

When sulfur burns in air a gas having the characteristic odor of burning matches is formed.

3. Determine whether the gas formed when sulfur is burned in oxygen is the same that is formed when it burns in air, by burning sulfur in a bottle containing air and in one containing oxygen, and compare the odors of the gases formed. Discuss the relation between combustion in air and in oxygen.

The difference in activity is due entirely to the fact that in air oxygen is diluted with another gas which does not support combustion.

REVIEW QUESTIONS

1. Describe the preparation of oxygen from potassium chlorate. Mention precautions to be observed.
2. What is the office of manganese dioxid in the above process?
3. What are the tests for oxygen?

4. Compare the action of oxygen on charcoal at ordinary temperatures with its action at high temperatures.

5. Compare the product obtained by burning charcoal in oxygen with the product obtained by burning it in air.

6. Compare the action of oxygen on phosphorus at ordinary temperatures with its action at high temperatures.

7. What can you say of the products of combustion in air and in oxygen?

8. Discuss the occurrence of oxygen in nature.

9. State the physical properties of oxygen; the chemical properties.

10. Does oxygen occur uncombined in nature?

11. Mention several compounds containing oxygen which occur in nature.

12. Does oxygen display greater energy at high temperatures than at low temperatures?

CHAPTER V

COMBUSTION

40. Ordinary Combustion. — In its broadest sense, the term combustion is applied to all cases of chemical action which are accompanied by an evolution of heat and light. In the majority of cases, however, oxygen is one of the elements concerned in combustion, and because of the rarity of the exceptions, the term is sometimes defined as the union of a substance with oxygen, accompanied by the evolution of heat and light; and the classification of substances as combustible and incombustible depends upon this definition of the term. Thus a combustible substance is one which unites with oxygen with evolution of light and heat, and an incombustible substance is one which cannot unite with oxygen.

Many substances are products of combustion; thus water is composed of hydrogen and oxygen, and carbon dioxid of carbon and oxygen. In these compounds the hydrogen and the carbon have already combined with oxygen, and cannot directly combine with more.

41. Kindling Temperature. — A wise provision of nature makes it necessary to raise the temperature of substances slightly above that which ordinarily obtains, to cause them to combine rapidly with oxygen. If this were not true we should have no fuels. Substances differ widely in the temperature to which they must be raised to cause them to combine with oxygen, but for each combustible substance

there is a definite temperature at which it combines with oxygen with sufficient energy to develop heat and light, and this is called the kindling temperature.

If the kindling temperature of a substance is below the ordinary temperature, it will take fire when it comes in contact with the air, and must, therefore, be kept out of contact with the air. Such substances are said to be spontaneously inflammable. Several substances have kindling temperatures below a red heat, *e.g.* the gaseous hydrogen phosphid may be ignited with a test tube containing boiling water, and the vapor of carbon disulfid may be ignited with a glass rod heated to 120°. Most solid fuels require a temperature slightly above redness, while the diamond must be raised to nearly a white heat before combustion begins. In starting a fire we take advantage of differences in the kindling temperatures of substances. For example, paper is easily ignited, but the heat which it develops cannot ignite the anthracite; hence we often put charcoal between the paper and the coal, as paper can ignite the charcoal. The use of a coating of sulfur or paraffin on matches, to enable the phosphorus to ignite the wood, is another instance of the use of a substance having an intermediate kindling temperature.

The temperature produced by the combustion of a substance is not necessarily the same as its kindling temperature. In all cases of ordinary combustion the temperature produced is higher than the kindling temperature of the substance; burning particles thus raise adjoining particles to the kindling temperature, and the burning continues without further application of heat when once started.

There are, however, numbers of cases in which the combustion cannot proceed without the continuous application of heat. The heat of the electric spark ignites nitrogen,

but the heat developed does not kindle the adjacent particles.

The facility with which a combustible substance may be ignited depends upon the quantity of heat, *i.e.* upon the number of heat units required to raise it to its kindling temperature. But, as we learn in physics, the temperature to which a substance is to be raised is only one of four quantities which determine the number of heat units required; the other three being the specific heat of the substances, its mass, and the number of heat units lost by conduction and radiation.

The amount of carbon to be kindled in a given stove depends upon the specific gravity and the porosity of the fuel; for example, charcoal, gas coke and anthracite coal are each of them nearly pure carbon, but they require very different amounts of kindling to ignite them. The specific gravity of the solid portions of these fuels are as follows: —

Pine charcoal	.40
Gas coke	.86
Anthracite	1.60

while the cell space or porosity expressed in cubic centimetres in 100 grammes of the fuel is as follows: —

Pine charcoal	200.4
Gas coke	60.
Anthracite	3.6

We thus see why charcoal requires comparatively little kindling to ignite it, although its kindling temperature is the same as the others.

The amount of heat lost by conduction has an important bearing on the amount of kindling required to build a fire. If the fuel is a good conductor of heat, it will be diffused throughout the mass, and such fuels are more readily

ignited if they are in small pieces, *e.g.* shavings are easier to ignite than a block of the same kind of wood.

Experiment XXXII. — Hold the laboratory burner horizontally over a sheet of white paper. Sprinkle some fine iron filings through the flame. What occurs? Pick up a few of the larger pieces on the paper and drop them through the flame again. What particles are raised to incandescence? Why?

Masses of metal in contact with the fuel often occasion considerable loss of heat by conduction. This action is nicely illustrated in the following experiment.

Experiment XXXIII. — Light a candle, bring a piece of wire gauze slowly down on the flame until it touches the wick. What occurs? Note the conditions above and below the gauze. Hold a lighted match above the gauze. What occurs? Explain. To what extent is the gauze heated? The Davy safety lamp used by miners illustrates this action.

42. Heat of Combustion. — It must be clearly understood that the light produced by combustion is due to the fact that the chemical action develops heat more rapidly than it can escape, thus raising the body to incandescence. There are many cases of oxidation, however, which take place slowly, or in which the substance is so situated that the heat is conducted away as fast as developed and in which a high temperature is not reached. The most important illustration of this action is the oxidation occurring within our bodies, which supplies the heat necessary to our existence. Other illustrations are found in the heat developed in compost heaps, in hotbeds, in the decay of wood, in cases of "spontaneous combustion," and in the rusting of iron.

The higher temperature acquired by a substance when it burns is readily accounted for by the difference in the *rate* at which it combines with oxygen. When two substances, such as carbon and oxygen, combine, their chemical affinity causes the atoms to rush toward each other, and the col-

lision which ensues increases their rate of vibration; that is to say, it develops heat. The *amount* of heat developed by the collision which forms a single molecule depends upon the magnitude of the attractive force and not upon the rate at which similar molecules are formed; it follows, therefore, that the oxidation of a given mass of a substance will develop exactly the same amount of heat when it burns that would have been developed if it had been oxidized slowly.

43. Chemical Energy. — All cases of direct chemical combination are due to attractions between unlike atoms; and whether the attraction be great or small, the collison of the atoms will develop heat. When molecules consisting of more than one atom act upon each other, the force which holds the atoms together in the original molecules must be overcome before a chemical change can occur; and the amount of heat developed in any reaction will accordingly depend upon the magnitude of the attractions of the atoms of the factors, as compared with the value of the attractions of atoms of the products. If the latter exceed the former, a chemical change will occur, accompanied by an evolution of heat. Chemical changes which evolve heat are known as *exothermic changes*, and those compounds which are formed from their elements by such changes are known as *exothermic substances*. Such substances are very stable, and when they are separated into their original elements the same quantity of heat that was evolved when they were formed disappears, or more exactly, is transformed into chemical potential energy. The formation of a much smaller class of substances is accompanied by the disappearance of heat; these are known as *endothermic bodies*, and when they are decomposed heat is evolved. They are usually unstable and often very explosive. All

endothermic substances possess chemical energy and can do work; that is to say, a substance which can combine with other substances without the aid of external energy possesses chemical energy. Much of the mechanical energy of the world is derived from endothermic substances, *e.g.* the fuels. The decomposition of carbon dioxid in the plant is an endothermic reaction in which the energy of the sunlight disappears. The carbon thus formed is stored up and may be again oxidized. For this reason the energy derived from wood and coal is sometimes spoken of as "stored sunlight."

44. Nomenclature of the Oxids. — The simplest chemical compounds are those composed of two elements only; they are known as *binary* compounds. Many binary compounds end with the letters *id;* but this rule cannot be depended upon in all instances.

Binary compounds of oxygen are called oxids; they are very numerous; *e.g.* oxygen forms five distinct compounds with nitrogen.

When there are two oxids of the same element it is quite common to distinguish them by adding the suffix *ic* to the name of the element to denote the oxid having the greater amount of oxygen, and the suffix *ous* to the name of the element to denote the oxid having the smaller proportion of oxygen. Thus, mercuric oxid has a larger percentage of oxygen than mercurous oxid, and nitric oxid a larger percentage than nitrous oxid.

If there are more than two oxids of the same element, prefixes are often used. Thus a *peroxid* contains a larger percentage of oxygen than the oxid to which the suffix *ic* is applied. Nitrogen peroxid, which contains a larger proportion of oxygen than nitric oxid, illustrates this usage.

A more scientific and simpler method of naming oxids

has been suggested, and is quite generally used. According to this plan the first part of the name of the oxid consists of the name of the element oxidized, and the second part of the name indicates the number of atoms of oxygen which the oxid contains, by the use of certain prefixes derived from the Greek. Oxids containing one atom of oxygen are called *monoxids, e.g.* carbon monoxid; those containing two atoms *dioxids, e.g.* carbon dioxid; those containing three atoms, *trioxids, e.g.* sulfur trioxid, etc.

45. Oxids in Nature. — Water, or hydric oxid is the most abundant oxid in nature, and sand (silicon dioxid) is next.

The ores of some of the most important metals are oxids, *e.g.* the red iron ore so common in this country is a compound of iron and oxygen, the molecule of which contains two atoms of iron and three of oxygen; and black iron ore, or lodestone, contains three atoms of iron and four of oxygen in its molecule. Many other ores are oxids, *e.g.* those of tin, manganese, etc.

REVIEW QUESTIONS

1. How do substances formed by burning in air compare with those formed by burning in oxygen?

2. Why is not combustion as rapid in air as in oxygen?

3. Define combustion. What are combustible substances?

4. Define kindling temperature. Which has the highest kindling temperature, sulfur, carbon, or phosphorus?

5. Mention examples of slow oxidation. How does slow oxidation differ from combustion?

6. Compare the amount of heat given off during slow oxidation and combustion.

7. What is meant by chemical energy? What substances possess it? What substances do not possess it?

8. From what source is the mechanical energy of wood derived? Explain.

9. What are oxids and how are they named? What do the terminations "ic" and "ous" indicate?

10. What important oxids occur in nature? Why are they so abundant?

11. Give evidences that a part of the air combines with the fuel in combustion.

12. Describe an experiment to show the relation of the weight of the products of a burning candle to the weight of the portion of the candle consumed.

13. How is combustion related to or distinguished from chemical action in general?

14. Mention conditions that favor combustion and chemical action in general.

15. Mention a condition favoring some chemical action but not combustion.

16. What is meant by kindling temperature? Explain the theory of shaving wood for use in starting a fire of the same kind of wood.

17. How does the chemical energy of the combustion of hydrogen compare with that of the combustion of other elements? Why?

18. Why is a fire of seasoned wood hotter than a fire of green wood?

19. Explain the use of sulfur in making the common friction match.

20. Why is a wood fire easily started with wood shavings?

21. Upon what does the temperature reached by combustion of a given quantity of fuel depend?

22. Mention five oxids occurring abundantly in nature.

23. Mention several substances which are acted upon by oxygen at ordinary temperatures.

24. Explain the effect of fine wire gauze when lowered over the flame of a lamp. Mention an important practical application of the principle involved.

25. Compare the kindling temperature of hydrogen with that of carbon. What bearing has their relative kindling temperature on the production of light by illuminating gas?

26. Explain the phenomenon of spontaneous combustion.

27. What would occur if the temperature developed by the combustion of nitrogen were higher than its kindling temperature?

CHAPTER VI

NITROGEN

Symbol N. — Atomic Weight 14

46. Occurrence. — Nitrogen forms $\frac{4}{5}$ of the bulk of the air. It is found in combination in a large number of substances, *e.g.* in saltpetre or potassium nitrate, KNO_3, and Chili saltpetre, $NaNO_3$. It also occurs abundantly in ammonia, nitric acid, flesh, and other animal substances. Its compounds give to burned hair and woollens their peculiar odor. Many vegetable substances contain nitrogen, as cabbage, mushroom, horse-radish, and it is an essential constituent of quinine, morphine, prussic acid, and strychnin. It forms a part of nearly all explosives, as nitroglycerin, gunpowder, etc.

47. Preparation. — Nitrogen may be prepared by removing the oxygen from the air. Any method which burns up the oxygen of the air and forms solid or liquid products, yields nitrogen which is reasonably pure. If any of the products are gaseous they will be mixed with the nitrogen, which will therefore be impure.

First Method. — Introduce a jet of burning hydrogen into a bottle of air. After the flame is extinguished there will remain in the bottle, nitrogen and the product of the combustion of hydrogen — H_2O.

Second Method. — Phosphorus burns in the air forming phosphorus pentoxid, P_2O_5, a flaky white substance which is soluble in water.

Experiment XXXIV. (See Experiment 28.) — Support a piece of chalk over water in the water pan by means of a wire standard. Make a hollow in the chalk, place a piece of dry phosphorus about the size of a pea in it. Ignite the phosphorus, quickly cover it with the large bottle so that the mouth of the bottle is under water. What chemical change takes place? Notice any change in the volume of the air. Explain. Does all the air support combustion? Take the bottle from the water pan (do not allow the water to escape) and shake it. What is the result? Does the white cloud which at first filled the bottle remain? Test the gas with a lighted taper. Is it combustible? Is it poisonous? State its physical properties.

Third Method. — If air be passed through a tube containing heated copper filings, the oxygen combines with the copper, forming copper oxid, and nitrogen may be collected. Nitrogen prepared from the air will contain the impurities which exist in the air. Pure nitrogen may be prepared as follows: —

Fourth Method. — Heat ammonium nitrite and collect evolved gas over water.

$$NH_4NO_2 = 2\,H_2O + 2\,N.$$

On account of the unstable character of ammonium nitrite, it is difficult to keep a supply on hand; in practice, therefore, a mixture of ammonium chlorid and sodium nitrite is usually substituted for the ammonium nitrite. When this mixture is heated the reaction proceeds according to the following equation: —

$$NH_4Cl + NaNO_2 = NaCl + 2\,H_2O + N_2.$$

This method supplies the purest nitrogen.

48. Physical Properties. — The last experiment taught us certain physical properties of nitrogen; mention them. The following additional physical properties not easily shown experimentally are worthy of consideration. It is sparingly soluble in water, only 1.6 % being dissolved at 10° C. It may be liquefied at — 193° under pressure of one atmosphere. It is slightly lighter than air.

49. Chemical Properties. — Nitrogen combines directly with very few elements, and combination with these elements is effected with difficulty. By indirect methods it can be made to combine with hydrogen, and with hydrogen and oxygen. Its chemical affinities are exceedingly feeble, and the compounds which it forms are very unstable. Gunpowder, nitroglycerin, and many other explosives are nitrogen compounds, and owe their characteristic properties to the ease with which they are decomposed. The rapid decay of animal and vegetable substances which contain nitrogen is a further illustration of the unstable character of nitrogen compounds.

REVIEW QUESTIONS

1. State the physical properties of nitrogen.
2. State its chemical properties, activity, combustibility, relation to explosives, relation to decay. Is it poisonous?
3. What proportion of the air is nitrogen? How is this shown?
4. Describe an experiment for obtaining nitrogen by the use of phosphorus. Give the name and formula of the fumes formed, and account for their disappearance.
5. Compare oxygen with nitrogen with respect to (*a*) chemical activity, (*b*) occurrence, (*c*) number of compounds, (*d*) relation to combustion and life, and (*e*) physical properties.
6. Why is nitrogen an important constituent of most explosives?
7. What are nitrogeneous foods?

CHAPTER VII

HYDROGEN

SYMBOL H. — ATOMIC WEIGHT 1

50. Occurrence. — Hydrogen is never found uncombined in nature; its compounds, however, are widely distributed. It forms $\frac{1}{9}$ of the weight of water, and occurs in all animal and vegetable matter. It is the only substance common to all acids.

51. Preparation by the Action of an Acid on a Metal.

Experiment XXXV. — 1. Put a few pieces of granulated zinc in the test bottle. Cover them with dilute hydrochloric acid. What occurs?

2. After a minute or two hold a lighted match over the bottle. What occurs?

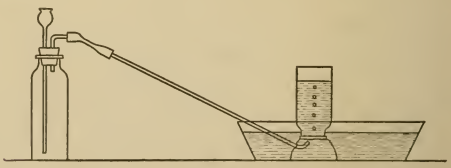


FIG. 4.

3. Put a few pieces of zinc in your generating bottle. In one hole in the rubber stopper put a straight glass tube long enough to reach to the bottom of the bottle; in the other fit a bent tube with a delivery tube attached. Pour enough dilute sulfuric acid into the bottle to cover the zinc. Collect the gas over water.

Caution. — The gas is explosive when mixed with air; when pure, it burns quietly. To determine when all the air which filled the bottle at the beginning of the experiment is driven off, collect a small bottle of gas; when full, raise it from the water, mouth downward, and apply a match. If the first bottle of gas explodes, repeat until a bottle of gas is obtained which burns quietly.

4. Collect three bottles of pure gas.

5. Place the first bottle, mouth upward and uncovered, on the table. After a few minutes, test it, to see whether or not it contains hydrogen. Is hydrogen lighter or heavier than air?

6. Pour the hydrogen in the second bottle upward into an inverted bottle containing air. Test each bottle with a match. Is there any hydrogen in the inverted bottle? In the other bottle?

7. Light a candle with a wire attached for a handle. Hold the third bottle mouth downward and thrust the lighted candle well into the bottle. What occurs? What burns? Does the candle burn? Withdraw the candle slowly. Is it alight? Why? Put it back into the hydrogen. Does hydrogen support combustion? Is the mouth of the bottle heated?

Experiment XXXVI. The Philosopher's Lamp. (Optional.) — Remove the delivery tube and substitute for it a tube drawn out to a fine point. If you are sure that the gas is pure, *i.e.* if you have not taken the stopper out of the generating bottle since testing the gas, light the gas at the end of the pointed tube. Hold a cold dry bottle over the flame. What do you see in the bottle? Where did it come from? (Chemical examination proves it to be pure water.) What is the product of the combustion of hydrogen?

Hydrogen may be prepared by several other processes; for example, by decomposing water by electricity (Experiment 40); by decomposing water by metals at ordinary temperatures (Experiment 42); by passing steam over heated metals (Art. 72, etc.).

The following equations represent chemical changes in the preparation of hydrogen by the action of an acid on a metal: —

$$Zn + 2\,HCl = ZnCl_2 + 2\,H.$$

This is the reaction when hydrochloric acid is used. If sulfuric acid is used, the following equation expresses the reaction: —

$$Zn + H_2SO_4 = ZnSO_4 + 2\,H.$$

52. Physical Properties. — Pure hydrogen is odorless, and is the lightest known substance; one litre of it at ordinary pressure weighing .08956 gramme. It may be liquefied by extreme cold and pressure, but is more difficult to liquefy than any other gas. It diffuses more rapidly than any other gas. Water dissolves only 2% of hydrogen.

53. Chemical Properties. — In its chemical affinities hydrogen closely resembles a metal; it has a strong affinity for oxygen, chlorin, and a few other elements, and the compounds which it forms with carbon indirectly are very numerous; it is, however, very difficult to get it to combine directly with carbon.

54. Comparison of Physical and Chemical Properties of Hydrogen and Oxygen. — Hydrogen will burn; oxygen supports combustion. Hydrogen has affinity for few substances; oxygen for many. Hydrogen is the lightest known substance. Oxygen combines readily with carbon, sulfur, phosphorus, and iron. It is difficult to get any of these elements to combine with hydrogen. The two elements have opposite chemical properties; yet in their physical properties they resemble each other.

55. Uses. — On account of its great affinity for oxygen, hydrogen is extensively used for the purpose of extracting oxygen from compounds containing it, *i.e.* as a reducing agent.

56. Heat and Chemical Energy of the Combustion of Hydrogen. — The chemical affinity of hydrogen for oxygen is

greater than that of any other known substance. The heat produced by the combustion of hydrogen is therefore greater than that of any other substance. One pound of hydrogen in burning gives off 34,400 heat units; that is, it develops enough heat to raise 34,400 pounds of water from 0° C. to 1° C.

The oxyhydrogen blowpipe consists of a tube *H* (Fig. 5), through which hydrogen flows, and at the end of which it is ignited. In the centre of this is a smaller tube

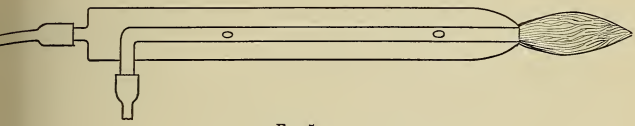


FIG. 5.

through which a stream of oxygen is forced into the flame. The flame produced gives very little light, but its temperature is between 2000 and 2200° C.; it is, therefore, used in working platinum and other metals fused with difficulty. A piece of lime held in the flame is heated to incandescence, and emits a bright light equivalent to about 120 standard candles. This device is known as the calcium light.

Experiment XXXVII. — Take notes on the effect of the oxyhydrogen blowpipe flame upon bits of lead, zinc, copper, steel, iron, glass, and calcium oxid.

57. Burning of Oxygen or Air in Hydrogen. — If a jet of oxygen or air be introduced into a vessel containing hydrogen, the oxygen or air may be ignited and will burn as readily as hydrogen burns in oxygen or in air.

If a stream of hydrogen be passed through the tube *H* (Fig. 6), and ignited at the bottom of the bottle, a jet of

air introduced through the hydrogen flame will burn with a flame of the same character as that produced when hydrogen burns in air.

58. Product of this Combustion. — The combustion of hydrogen must form an oxid of hydrogen. Water is an oxid of hydrogen, and analysis of the moisture condensed on any cold object held over the hydrogen flame, proves that water is the product.

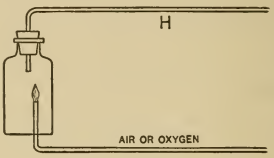


FIG. 6.

59. Formation of this Substance in Ordinary Combustion. — Nearly all fuels contain hydrogen, and therefore form more or less water when they burn; this can be shown by holding a cold object over the flame. Moisture can thus be condensed over burning oil, wood, coal, gas, etc. When oxygen combines with the waste products of the body in the lungs, the hydrogen of the products is turned into water; thus the well-known cloud formed by the breath in cold weather is this moisture rendered visible by condensation. This may be easily shown by breathing upon any cold dry object.

REVIEW QUESTIONS

1. Explain the cause of the moisture which appears on a lamp chimney when the lamp is lighted.
2. Why does this film disappear?
3. If water is a product of combustion, why does it not extinguish the fire?

4. State the symbol, atomic weight, and occurrence of hydrogen.

5. Describe the process of preparing hydrogen from zinc and hydrochloric acid. Write the reaction.

6. Discuss the physical and chemical properties of hydrogen.

7. Describe the oxyhydrogen blowpipe. For what is it used?

8. Show how a jet of air may be burned in hydrogen.

9. What does the moisture which gathers on a cold object held over a lighted kerosene lamp indicate as to the composition of the kerosene oil?

10. Discuss the heat and chemical energy of the combustion of hydrogen.

11. State the color and odor of the gas prepared in Experiment 35.

12. Is hydrogen explosive? Under what conditions?

13. Does hydrogen combine with oxygen at ordinary temperatures? at high temperatures?

14. Describe the hydrogen flame as to (*a*) color, (*b*) amount of heat, (*c*) amount of light.

CHAPTER VIII

CHEMISTRY OF WATER

FORMULA H_2O. — MOLECULAR WEIGHT 18

60. Occurrence of Water in Nature. — Three-fourths of the earth's surface is covered with water. It exists in the atmosphere, in all vegetable and animal matter, in the soil, and even in the rocks.

Experiment XXXVIII. — Heat a small piece of alum in a test tube. Note evidence that it contains water. Is the loss of water accompanied by a change in the crystal? Explain. Repeat the experiment, using pieces of gypsum, meat, potato, etc.

61. Properties of Water. — At ordinary temperatures pure water is a tasteless, odorless, transparent fluid, colorless in thin layers, but distinctly blue when viewed in large masses. At its greatest density water is 773 times heavier than air.

Many of the properties of water are used as standards by means of which we may express the corresponding properties of other substances. The specific gravity of all solids and liquids expresses the relation between the weight of the substances and the weight of a like volume of water.

The specific heat of all substances is similarly based upon that of water. In the metric system the unit of weight is the weight of a cubic centimetre of water, and the melting and boiling points of water are the standard temperatures used in the manufacture of thermometers.

62. Solution. — Water dissolves a greater number of solid, liquid, and aeriform substances than any other solvent.

The adhesion between the molecules of the dissolved substance and those of water overcomes the cohesion of the substance dissolved, and it diffuses through the mass of water, forming a transparent *solution* in which the dissolved substance is invisible. Strongly colored substances, however, impart their characteristic color to the solution. There is a limit to the amount of a substance which a solvent can dissolve at a given temperature and pressure, and a solution which contains all of a substance which it can dissolve is said to be *saturated.*

We can now understand why solution aids chemical action. The molecules are no longer held firmly together by cohesion; they are free to move, and are thus easily brought into the intimate contact necessary to chemical action by their chemical affinities.

If sugar is dissolved in water the solution seems to be simply a mechanical mixture; there is no evidence that a chemical change has taken place; and if the solution is evaporated the sugar is recovered unchanged. This, therefore, is a *physical solution.*

In Experiment 9, marble was dissolved in hydrochloric acid and a chemical change was proven. Such solutions are called *chemical solutions.*

63. The Effect of Heat on the Solution of Solids and Gases.— Physics teaches us that whenever a solid changes to the liquid form a certain quantity of heat is rendered latent. Hot water can supply this heat more readily than cold, and therefore solids are more rapidly dissolved by hot than by cold water. Furthermore, a larger quantity of most solids is dissolved by hot water than by cold. At high temperatures the cohesion of the molecules of a solid is less than at low temperatures, therefore there is less force to overcome

in dissolving it. As the water cools, latent heat is withdrawn from a certain quantity of the dissolved substance, causing it to assume a solid state.

When a gas is dissolved in a liquid its latent heat must be absorbed, but a cold liquid can absorb heat more rapidly than a warm one, and therefore a gas is more rapidly dissolved in a cold liquid than in a warm one. As the temperature of a solution of a gas is raised, a portion of the heat is used to change the state of the dissolved gas and a portion is liberated in gaseous forms.

64. Water of Crystallization. — Experiment 38 taught us that crystalline alum contained water, and that the alum lost its geometrical form when the water was driven off. Many other crystals are like alum in this respect, and there is evidence that the water which they contain is held in feeble chemical combination. The water of crystallization does not make the substance moist, as it would if absorbed mechanically, and further, a given substance requires a definite amount of water for each molecule of the crystal. Certain substances form two or more kinds of crystal, requiring different quantities of water; and in some crystals the color depends upon the amount of water of crystallization. Cobalt chlorid is often used as a *sympathetic ink* because of the change in color produced by expelling the water of crystallization.

In some crystals the water is held so feebly that they lose either the whole or a portion of their water of crystallization when exposed to the air, and in so doing lose their particular geometrical form. This process is known as *efflorescence.*

Other crystals absorb water from the air and assume other geometrical forms, in some cases absorbing enough water to dissolve the crystal. Such crystals are said to be *deliquescent.*

Experiment XXXIX. — Put a crystal of ferrous sulfate and a small piece of calcium chlorid on separate pieces of paper and expose them to the air for several days. Which is efflorescent? Which deliquescent?

65. Hydroxids. — Strictly speaking hydroxids are compounds formed by replacing one atom of hydrogen in the molecule of water with an atom of another element or with a group of elements.

$$Na + H_2O = NaOH + H$$
$$CaO + H_2O = CaO_2H_2.$$

According to this definition most acids are hydroxids but chemists rarely apply the term to them, whereas, all chemists agree in calling a compound formed by the union of a metal with hydrogen and oxygen an hydroxid.

These compounds, which are very important and which are discussed more fully in Chapter XII., are sometimes called hydrates, but the term is rather objectionable because the termination *ate* is used to distinguish a class of compounds to which the hydroxids do not belong.

66. Electrolysis of Water.

Experiment XL. (Performed by the instructor.) — Take notes upon this experiment, answering all the following questions and describing the apparatus used. An electric current is passed through acidulated water from one lead or platinum electrode to another. Gas is evolved which is collected in two tubes. Where is the gas liberated? How does the volume over the positive electrode compare with that over the negative? What gas is collected over the positive electrode? How do you know? What gas is collected over the negative electrode? Does this experiment prove that water is composed of two elements and no more? Is the volume of the water decomposed equal to the volume of the gases formed? How do you know?

67. Synthesis of Water.

Experiment XLI. (Performed by the instructor.) — Eudiometer tube — a "U" shaped tube of glass about 18 inches long closed at one end, having two platinum wires inserted at opposite sides near the closed

end. Fill the eudiometer tube with mercury and invert in a mercury bath. Introduce a certain amount of oxygen, removing the tube and bringing the mercury to a level in both arms. Read the amount of oxygen in the tube, filling the arm with mercury again. Introduce about twice as much hydrogen in a similar manner, determining the exact volume, placing the thumb over the end of the tube that is open, and wrapping the tube in a towel, pass an electric shock through the wire. An explosion occurs, and water is formed. Some of the gas remains in the tube. Testing this residual gas to determine whether it is hydrogen or oxygen and subtracting its volume from the quantity used, we determine the volume of the two gases which combined.

This experiment proves that there are only two elements in water.

68. Formation of Water by passing Hydrogen over Heated Oxid. — When mercuric oxid is heated, oxygen is liberated. If a stream of hydrogen be passed over a heated oxid, the hydrogen and oxygen combine to form water. When copper oxid is used, the following reaction takes place: —

$$CuO + 2H = Cu + H_2O.$$

In this experiment if the weight of water formed be determined and the tube containing copper oxid be weighed before and after the heating, it will be found that $\frac{8}{9}$ of the weight of water came from the copper oxid, thus proving that $\frac{8}{9}$ of the weight of water is oxygen.

69. Composition of Water by Weight and by Volume. — Preceding experiments have shown that water contains twice as much hydrogen as oxygen, *volume* alone considered, and that it contains eight times as much oxygen as hydrogen, *weight* alone being considered. These two seemingly contradictory facts being proven, it follows that the single volume of oxygen must be eight times as heavy as the two volumes of hydrogen, and that equal volumes being considered, the oxygen is sixteen times as heavy as the hydrogen. In considering the composition of a compound, care must be taken to distinguish between these two

methods of stating the composition, and it must be remembered that the volumes used are, in all cases, the volume in an aeriform state, and not the solid or liquid state. One further fact should be stated here: when two volumes of hydrogen combine with one volume of oxygen to form water they do not form three volumes of steam; their volumes is condensed one-third, so that —

2 vols. of hydrogen + 1 vol. of oxygen form 2 vols. of steam,

and this is the way in which the composition of a substance by volume should be stated. For further discussion of this topic see p. 118.

The composition of a substance by weight is the same in the solid as it is in the liquid and aeriform state. That of water may be stated thus: —

2 parts (by weight) of hydrogen + 16 parts of oxygen form 18 parts of water.

70. Decomposition of Water by Metals.

Experiment XLII. — 1. Fill a medium sized bottle with water and invert it in the yellow dish, which should be about half full of water.

2. Thoroughly dry a small piece of wire gauze in the gas flame, roll around a lead pencil, so that it forms a cylinder that is double walled in all parts. Fold one end of the cylinder over and pinch the bend with a pair of pliers. Drop a piece of sodium the size of a pea into it, using the pliers as before.

3. Lift the bottle slightly, but not enough to allow the water to escape, and thrust the wire gauze beneath it. After all action has ceased slip a glass plate under the mouth of the bottle and remove the bottle from the water pan, placing it right side up on the table.

4. Test the gas with a burning match. Do you recognize the gas? How? Where did it come from? Drop a piece of pink litmus paper in the bottle. Does it change color? Does water from the laboratory faucet produce a similar change? What became of the sodium.

Explain concisely all that has occurred. The reaction is as follows: —

Sodium + Water = Sodium Hydroxid + Hydrogen

$$Na + H_2O = NaOH + H$$

NOTE. — Litmus paper is prepared by dipping strips of paper into an infusion of litmus. It turns red, when treated with an acid, and blue, when treated with an alkali.

71. Decomposition of Water by passing Steam over Heated Metals. — Certain other metals which decompose water slowly or not at all at ordinary temperatures, decompose it easily at high temperatures. If steam be passed through a tube containing bits of iron heated to redness, it will be decomposed and hydrogen may be collected over water.

$$3\,Fe + 4\,H_2O = Fe_3O_4 + 8\,H.$$

QUERY. — How may the weights of hydrogen and oxygen resulting from the decomposition be determined in this experiment?

72. Water Gas. — At high temperatures carbon also decomposes water, and this fact is the basis of the process of manufacturing water gas. Steam is passed over highly heated coal or coke (carbon), which combines with the oxygen of the water, forming carbon monoxid (CO). The reaction is as follows: —

$$C + H_2O = CO + 2\,H.$$

Both carbon monoxid and hydrogen are combustible gases, they are both odorless, and burn with feebly luminous flames. To overcome these objections it is customary to enrich water gas by adding certain gases, obtained by decomposing naphtha, which give the gas a distinct odor, and which greatly increase the amount of light produced. The illuminating gas used in many of our cities is prepared by this process, but the increased value of the ammonia and of the tar obtained as by-products in the process of manufacturing illuminating gas from bituminous coal has rendered the economy of water gas questionable. As water gas is more poisonous than ordinary illuminating gas, laws have been passed in certain states prohibiting its use.

73. Oxidation and Reduction. — The process of abstracting oxygen from a body is called *reduction.* In the manufacture of water gas the hot carbon abstracts the oxygen from the water, illustrating its use as a reducing agent. Carbon is extensively used in the reduction of ores to a metallic state. The union of a substance with oxygen is called *oxidation,* and the reagent which causes the oxidation is called the *oxidizing agent.* Nitric acid and potassium chlorate are excellent oxidizing agents, as will be noticed in several subsequent experiments. In Experiment 42 the sodium was oxidized by the water, but water is not among the better oxidizing agents.

74. Natural Waters. — Absolutely pure water is never found in nature. The impurities which it contains are of two classes: first, the *inorganic,* or those derived from the rocks; and second, the *organic,* or those derived from the decay of animal matter or vegetable substances. Some of the impurities are held in solution, while others are suspended and carried along by moving water. The purest water found in nature is rain water, particularly that which falls in country districts after it has been raining some time. But even rain water contains impurities; as it falls through the air it washes it, removing those suspended matters which are always present in it, and dissolving small quantities of the gases of the atmosphere. As soon as the rain reaches the earth, its great solvent power is exerted upon the mineral matter with which it comes in contact, and it becomes more impure. An impure water is not necessarily unfit for household purposes. See Article 78.

75. Spring Water always contains dissolved mineral matter as well as a considerable quantity of carbon dioxide derived from the decomposition of plants. Waters flowing

through different strata would naturally contain different amounts and different kinds of minerals, and we therefore have various kinds of spring waters. *Sulfur springs* usually issue from rocks containing a decomposing sulfid. A line of sulfur springs across western New York marks the outcrop of the Hamilton shale which, in certain layers, contains a great deal of iron sulfid. The *chalybeate springs* contain some compounds of iron in the same way, and the *effervescent waters* have some gas in solution. The famous springs at Saratoga, N.Y., belonging to this class, contain carbon dioxid.

76. River water differs from spring water because a part of it, at least, has not been filtered through porous rock and thus relieved of suspended matter. It is consequently turbid, while spring water is usually clear and sparkling. Sea-water contains a large amount of mineral matter, the average quantity being about 3.5 % of its weight.

77. Hard Water. — Certain salts which are frequently present in natural waters prevent the formation of a lather with soap in the ordinary process of washing, and give to waters containing them the property known as hardness. The chief substances which produce this effect are the compounds of calcium and magnesium. Soap is decomposed by such waters, forming an insoluble, curdy precipitate or scum which prevents the cleansing action of the soap until all of the hardening salts have been removed. Hardness due to the presence of carbonates may be removed by boiling the water, and is called *temporary hardness.* Waters having this kind of hardness are common in limestone regions. The limestone is an impure calcium carbonate ($CaCO_3$), and is not soluble in water, but water containing carbon dioxid converts the calcium carbonate into an acid carbonate ($CaH_2(CO_3)_2$) which is soluble. *Permanent hard-*

ness, or that which remains after prolonged boiling, is usually due to the presence of sulfates.

78. Potable Waters. — The inorganic impurities found in natural waters are very rarely injurious to health. The organic impurities, however, are usually accompanied by living germs, or bacilli, by means of which such diseases as cholera, typhoid fever, diphtheria, etc., are propagated. The principal source from which these dangerous organic impurities are derived is the drainage of houses and villages; and though waters thus contaminated may become pure again through the action of the air and sunlight, it is not safe to rely upon this method of purification in the water which is to be used for drinking purposes.

It is of the greatest importance that the water used for drinking purposes should be as pure as possible; to this end it should be frequently tested, and if there is the slightest suspicion of contamination, it should be thoroughly boiled.

In general it may be assumed that springs, deep wells, and mountain rivers and lakes, are safe sources of water supply; that stored rain water and surface water from cultivated land are unreliable; and that shallow wells and rivers, to which sewage gains access, are dangerous sources.

79. Distillation and other Methods of Purification. — The best method of purifying water is by distillation. This process removes both organic and inorganic impurities; and, when properly conducted, supplies a perfectly pure water. On shipboard the salt water of the ocean is distilled.

Experiment XLIII. — Using a flask, distil 30 or 60 cc. of water. Under "Physical Properties" note color, taste, odor. What action has it upon litmus paper? Does it leave a residue upon evaporation? Answer same questions concerning some natural water.

Boiling. — Thoroughly boiling water, renders most of the organic impurities harmless. Disease germs are destroyed

and albuminous matter coagulated so that it may be readily removed by filtration.

Filtration does not remove the dissolved inorganic impurities, — these can be removed only by chemical processes (see next article); but when properly conducted it removes both organic and inorganic suspended matter, including disease germs.

Small *charcoal* or *sand filters* are more apt to contaminate the water passing through them than to purify it; for after a few days' use, the filter becomes so saturated with germs that the filtered water contains more of them than it did before it was filtered. Unless the filter is so constructed that the charcoal or sand may be removed and exposed to air and sunlight, it is unsafe to use it. The wire strainers, sometimes called filters and made to be attached to faucets, may remove some of the suspended matter, but they do not remove the germs. The *Pasteur filter*, in which the water passes through a natural stone, is the most efficient small filter; the stone must be removed and boiled, or exposed to the air for oxidation of the organic matter, occasionally, otherwise germs will pass through the filter after a time.

Chemical Methods. — Attempts are rarely made to purify water on a large scale by chemical processes. But such processes have been employed for many years by frontiersmen and in regions where no drinkable water exists.

If alum is gradually added to impure water containing calcium carbonate, calcium sulfate is formed, carbon dioxid is evolved, and aluminum hydroxid is precipitated. The aluminum hydroxid entangles the organic matter present and settles with it to the bottom, leaving the water clear and sparkling. If the water contains an insufficient amount of calcium carbonate, it will not be rendered perfectly clear, and the deficiency must be supplied by adding sodium carbonate.

Ferric chlorid, iron borings, and potassium permanganate have each been used successfully in chemical processes of purifying water.

80. Softening. — (*a*) *Temporary Hardness.*

Experiment XLIV. — 1. Dissolve 1 gramme of soap shavings in 10 cc. of distilled water in a test tube. Draw out one end of a glass tube, about $\frac{1}{4}$ inch in diameter, to a point thus: —

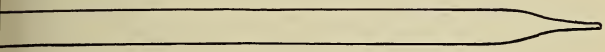


Fig. 7.

This is to be used as a dropping tube.

2. Test 10 cc. of hard water, made by passing carbon dioxid through lime water until it is clear, in a test tube as follows: Using the dropping tube, add a single drop of the soap solution to the hard water, shake the tube, repeat the operation as often as may be necessary to determine the number of drops required to produce frothing.

3. Test 10 cc. of distilled water in the same way. What do you conclude concerning the relative values of hard and pure water for washing purposes?

4. Boil some of the hard water and test 10 cc. as before. How does this compare in value with the unboiled sample?

Boiling decomposes the soluble carbonates, expelling carbon dioxid and precipitating the insoluble carbonate. The "fur" which forms on the bottom and sides of the tea-kettle and the scale which forms on the shell and tubes of a steam boiler are each due to the repeated removal of carbonates from water by boiling.

Clark's process of removing temporary hardness is quite extensively used by water-works engineers. The hardness is estimated, and the quantity of "milk of lime" required to transform the amount of soluble carbonate present into insoluble carbonate is then added. The reaction is as follows: —

$$CaH_2(CO_3)_2 + CaO = H_2O + 2\,CaCO_3.$$

(*b*) *Permanent Hardness.*

Experiment XLV. — 1. Test 10 cc. of hard water, made by dissolving calcium sulfate in distilled water and filtering, as in Experiment 44. Note the number of drops of soap solution necessary to produce frothing. Boil some of the above-mentioned hard water, and test as before. What effect does boiling have on permanent hardness?

The sulfates and chlorids of lime and magnesium are decomposed by sodium carbonate (common washing soda) with the following reaction: —

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

The sodium sulfate produced has no effect on the soap, but water containing it should not be used for drinking purposes. Hence the use of washing soda for softening water.

81. Natural Methods of Purification. (*a*) *Action of the Air.* — Disease germs die when exposed to the sunlight, and organic impurities are oxidized when exposed to the air. Therefore, impure water running through shallow streams, or over precipices in a thin sheet, tends to become pure again.

(*b*) *Filtration* through beds of sand or porous rock removes suspended matter. It is in this way that most spring waters are rendered clear and transparent; it should be remarked, however, that clearness is not unfailing evidence that water is healthful.

(*c*) *Sedimentation.* — In ponds and lakes water is often rendered clear, the suspended matter settling to the bottom under the influence of the force of gravity.

(*d*) *Natural Distillation.* — This is the most important method of purifying the water in nature. The sun is the source of heat, and since evaporation takes place at a temperature far below the boiling point, it occurs everywhere and at all times, even in winter, and the amount evaporated every hour is enormous. The vapor rises to the upper atmosphere, and encountering cold currents is

condensed in microscopic particles which float in the air. These increase in size as they move about, and finally fall as rain. The purest water found in nature is rain water, particularly after it has rained some time.

Mountain streams which flow over rocky beds, notably those which flow over beds of sandstone, have exceptionally pure waters. Water which flows over limestone dissolves some of the stone and becomes hard.

NOTE. — It is suggested that students take advantage of the opportunity offered by Experiments 46–48 to examine the water which they habitually use for drinking purposes.

82. Tests for Organic Impurities.

Experiment XLVI. — Fill a tall glass jar with water to be tested. Add a few drops of sulfuric acid, then add a weak solution of potassium permanganate, drop by drop, until the water assumes a violet tint. If organic matter be present, the color gradually grows lighter. If the color remains unchanged for an hour, the water may be considered safe for drinking purposes.

Nessler's Test. — Nessler's reagent is prepared by mixing potassium iodid and mercuric chlorid, and adding caustic soda. It furnishes a very delicate test for free ammonia, which is evidence of decomposing organic matter.

A drop or two of the reagent added to water containing ammonia gives it a brown color; the greater the amount of ammonia, the darker the shade of brown. In practice it is customary to concentrate the ammonia in 500 cc. of the water to be tested by distilling it with a small quantity of sodium carbonate, and testing the first 50 cc. of the distillate with Nessler's reagent.

Experiment XLVII. Test for Chlorids.

NOTE. — The members of the class should secure samples of drinking water from as many sources as possible, including water from a shallow well, a deep well, a pond, and a stream. Distilled water and a solution of common salt will be required; these are for comparison only, as distilled water contains no chlorin, and salt water a great deal. (Common salt is composed of sodium and chlorin.)

1. Add a few drops of nitric acid, free from chlorin, to 25 cc. of the distilled water, then add a few drops of silver nitrate solution.

2. Treat 25 cc. of the salt water in the same way. Compare this

with the distilled water. How can you distinguish water containing chlorin from pure water?

3. Concentrate 50 cc. of the drinking water to be tested to 25 cc. by boiling, and repeat the test.

Does it contain chlorin? Compare your result with that of other members of the class, and answer the following questions: —

Does the water from the shallow well become milky? Does that from the deep well? Which samples contain chlorin?

Sewage always contains chlorids, and hence if a drinking water is found to contain a chlorid, it is to be suspected, and the chlorin must be *proved* to come from some other source, or the water should be avoided. If a well is sunk near the sea, or near a deposit of rock salt, its water may be perfectly wholesome although containing a relatively large amount of chlorids.

83. Tests for Inorganic Impurities. — The presence of inorganic impurities is usually made known without a chemical test; the presence of hydrogen sulfid is detected by the odor, free carbon dioxid by effervescence, iron by the taste, and dissolved salts by the action of soap.

The presence of solids in solution may be determined by evaporating a few drops of the water to be tested on clean platinum foil. If solids be present, a residue will remain on the foil.

The fact that one usually desires to know concerning the inorganic impurities of water supplied for household use is its degree of hardness.

Experiment XLVIII. To determine the Degree of Hardness. — Pour 70 cc. of the water under examination into a flask. Add 1 cc. of "Clark's soap solution," insert a stopper, and shake thoroughly. Set it aside for two or three minutes; if a lather does not remain on the surface of the water at this time, add a second cubic centimetre of the soap solution. Repeat this process until a permanent lather is obtained. The number of cubic centimetres of soap solution used is equal to the number of degrees of hardness, and is one greater than the number of grains of calcium carbonate per imperial gallon.

22. A litre of water weighs 1000 grammes; how many grammes of hydrogen does it contain? how many grammes of oxygen? how many litres of each?

23. How many litres of the element in the first column may be obtained from 10 grammes of the substance in the second column?

H	H_3SO_4
O	H_2SO_4
O	HNO_3
H	HNO_3
N	HNO_3
H	HCl
Cl	HCl

24. How many grammes of the substance in the first column will be required to prepare 10 litres of the element in the second column?

H_2SO_4	
$KClO_3$	Cl
$KClO_3$	O
Zn	H
H_2O	O

CHAPTER X

COMPOUNDS OF NITROGEN AND HYDROGEN

Nitrogen combines with hydrogen to form three compounds; namely: —

Ammonia,	NH_3
Hydrazine,	N_3H_4
Hydrazoic acid,	N_3H

AMMONIA

Formula NH_3. — Molecular Weight 17

90. Occurrence. — Ammonia occurs in small quantities in the air, being formed under certain conditions by the decay of animal and vegetable substances.

The chief source of ammonia is the ammoniacal liquor of the gas works, which is the water through which the gas has been passed to remove the ammonia formed by the decomposition of the coal.

91. Preparation of Ammonia, NH_3.

Experiment XLIX. (For two students.)

Note. — Experiment 50 may be performed with this one if the students will arrange the three bottles with tubes required before beginning this experiment.

1. Mix 4 grammes of ammonium chlorid and 8 grammes of calcium hydrate on a piece of glass, adding a few drops of water. Place the mixture in a flask with a suitable delivery tube, add sufficient water to cover the mass, and apply heat.

2. Collect three bottles of the gas by upward displacement. Set them aside, mouth downward.

3. Hold the Bunsen burner flame in a stream of the gas. Can you ignite it? Does the gas burn while the burner is held in the stream? Is the gas combustible? Can its flame be said to have a color?

4. Connect the flask to the series of bottles described in Experiment 50, and proceed with that experiment.

5. When leisure permits, test the three bottles of the gas in such manner as to enable you to answer the following questions: —

Is it a supporter of combustion? Is it heavier or lighter than air? Is it soluble in water? Test with a piece of moist pink litmus paper. Note the odor. CAUTION.

When ammonia is prepared as above, the action is as follows: —

$$CaH_2O_2 + 2\,NH_2Cl = 2\,NH_3 + CaCl_2 + 2\,H_2O.$$

Ammonia is also formed when nitrogenous organic matter is heated out of contact with the air, as in the process of making illuminating gas by heating coal, or in the process of making animal charcoal.

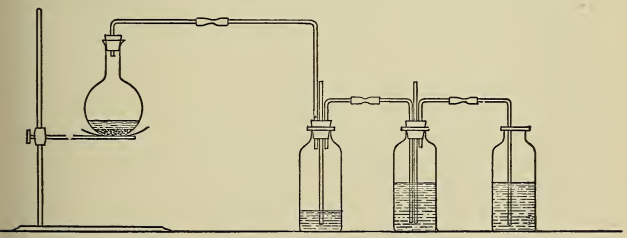


FIG. 8.

Ammonia gas is often prepared by heating the stronger ammonia water of commerce in a flask and collecting the gas as in Experiment 49.

Ammonia water was formerly called spirits of hartshorn, because it was prepared by distilling the horns of the hart.

92. Preparation of Ammonium Hydroxid, NH_4OH (Ammonia Water).

Experiment L. (For two students.) — 1. Connect a series of three medium sized bottles with the delivery tube of the flask used in Experiment 49 as shown in Fig. 8. Have 20 cc. of water in the first bottle, and about 50 cc. in each of the others. The first and second bottles are fitted with rubber stoppers. Neither tube of the first bottle should dip below the water. The tubes by which the gas enters the remaining bottles should dip beneath the water. The gas is sometimes dissolved faster than it is supplied in a given bottle, and a vacuum is formed, causing the water to run into it from the next bottle. Should this occur, raise the stopper of the bottle toward which the water flows. If three-holed stoppers are at hand, it is best to use them, and to insert safety tubes in the first and second bottles, thus preventing this action.

2. Hold a glass rod moistened with hydrochloric acid over a bottle of ammonia water. What occurs? This is the test for ammonia. Test the ammonia water with litmus paper.

93. Manufacturing Processes. — In the arts, ammonia is prepared either by adding slaked lime to the ammoniacal liquor of the gas works, or by boiling the liquor. In

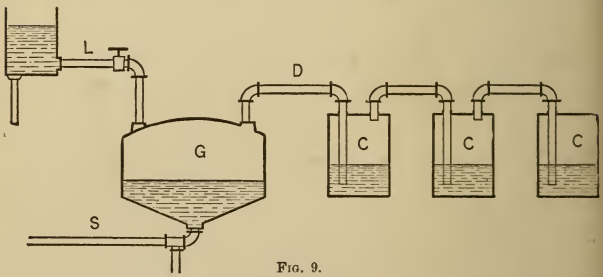


Fig. 9.

the latter process the vapor is often passed into sulfuric acid, forming crude ammonium sulfate, which is used as a fertilizer.

At the Rochester Ammonia Works the liquor is forced

into the generator *G*, Fig. 9, by a steam siphon *S*, and slaked lime is introduced through the pipe *L*. The mixture is agitated and heated, and the gas escapes through the delivery pipe *D* to the iron tanks *C*, where it is dissolved in water as in Experiment 50. Between *G* and *C*, the gas passes through several cylinders containing petroleum and various other solvents which absorb impurities, but allow the ammonia to pass through them. In this way, the "stronger ammonia water" of the drug stores is made.

94. Liquid Ammonia. — There is a large demand for anhydrous ammonia for use in ice machines. It is usually prepared as follows: Ammonia water is heated in an iron cylinder *A*, Fig. 10. The gas, NH_3, is driven over into the condenser *C*. As it accumulates, the pressure increases until it reaches 130 pounds per square inch, when the gas is liquefied.

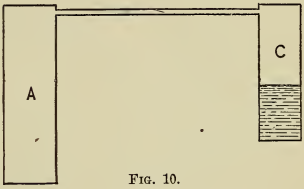


FIG. 10.

95. Physical Properties. — Ammonia gas can be easily condensed to the liquid form by cold and pressure. When the pressure is removed it passes back to the form of gas and absorbs heat in so doing.

One volume of water dissolves 600 volumes of ammonia gas at ordinary temperatures. It condenses at ordinary temperatures at 6.9 atmospheres; at ordinary pressures it boils at $-33.7°$ C. and solidifies at $-75°$.

96. Chemical Properties. — A jet of ammonia to which a flame is applied continues to burn in oxygen after the flame is withdrawn. In air, however, the heat of com-

bustion is not sufficient to raise adjoining particles to the kindling temperature.

In gaseous form as well as in the solution ammonia turns red litmus paper blue and neutralizes acids just as the alkalies, sodium, and potassium hydroxids do.

Ammonia combines directly with acids and many other substances to form a series of compounds which resemble each other in general properties, and each of which contains the group of atoms NH_4. In its chemical action, therefore, this group resembles a metallic element, and in order to distinguish it from ammonia, NH_3, the termination *um*, which is applied to nearly all metallic elements, is substituted for the final *a* of ammonia. The similarity in composition of some of the compounds of ammonium, zinc, and sodium is shown in the following table: —

NH_4	Zn	Na
NH_4Cl	$ZnCl_2$	$NaCl$
$(NH_4)_2SO_4$	$ZnSO_4$	Na_2SO_4
NH_4NO_3	$Zn(NO_3)_2$	$NaNO_3$

Compounds which play the part of an element are called *radicals.*

There is more or less evidence that a definite chemical compound is formed when ammonia is dissolved in water and that its formula is NH_4OH. This compound has never been isolated, however, and certain chemists doubt its existence. The name ammonium hydroxid implies that the solution is chemical rather than physical.

97. Uses. — Ammonia is extensively used in the manufacture of artificial ice, aniline colors, indigo, washing soda,

etc. It is also used in the laboratory as a reagent and in the household as a detergent.

The following device illustrates the manner in which liquid ammonia is employed in making artificial ice: —

Anhydrous ammonia flows from the tank *LA* into the chamber which surrounds a vessel of water *I*; it evaporates rapidly, and so much heat is rendered latent that the water is frozen. The gas is pumped back into the tank and again liquefied by pressure, and the operation is repeated.

In the Carre Ice Machine, a pound of coal is consumed for each pound of ice made.

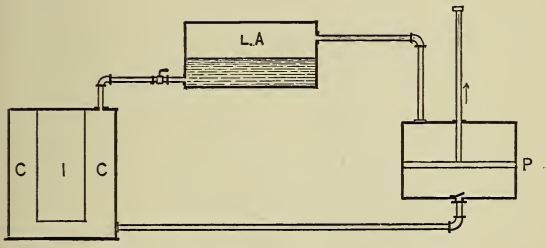


Fig. 11.

REVIEW QUESTIONS

1. Describe the preparation of the ammonia of commerce.
2. Describe the preparation of ammonia in the laboratory.
3. Discuss the combination of ammonia with water.
4. Distinguish between ammonia and ammonium; between liquid ammonia and ammonia water.
5. In what respect does ammonium resemble a metal?
6. What is hartshorn?
7. State the color, odor, solubility, and weight of ammonia.

CHAPTER XI

NITRIC ACID

FORMULA HNO_3. — MOLECULAR WEIGHT 63

98. Occurrence. — Nitric acid is formed in the air in small quantities during thunder storms, and is washed to the earth by rain, where it combines with elements found in the soil.

The compounds of nitric acid and the metals potassium and sodium occur abundantly in certain localities, particularly in India, where the waste products of animal life found near the villages are rapidly oxidizing, forming potassium nitrate (saltpetre), and in a desert tract in Chili, where the oxidation forms sodium nitrate, or Chili saltpetre. It has been suggested that this tract was at one time covered by the sea, and that the nitric acid was formed from the oxidation of sea-weeds and animals.

In the economy of nature no substance, however obnoxious, is lost, and the formation of these nitrates illustrates one method by which the vast army of living organisms in the soil converts waste material into useful and wholesome forms.

99. Preparation. — Nitric acid is prepared by distilling either potassium or sodium nitrate with sulfuric acid.

Experiment LI. — Place 15 grammes powdered potassium nitrate in a flask. Add 10 cc. strong sulfuric acid. Heat the flask on a sand bath, and condense the vapor in a test tube placed in a bottle of cold water. As the mixture begins to boil, drops of liquid will form on the

sides of the flask and run down into the mixture. After a short time the lower part of the flask appears dry, and the drops of liquid are observed on the neck of the flask. As the action progresses, more and more of the flask appears to be dry. Explain this action. Describe the acid obtained as to state, color, odor, action on litmus. Describe the substance which remains in the flask.

100. Reaction. — At high temperatures the following reaction occurs: —

$$2\,KNO_3 + H_2SO_4 = 2\,HNO_3 + K_2SO_4.$$

If the temperature be lower, the reaction becomes: —

$$KNO_3 + H_2SO_4 = HNO_3 + HKSO_4.$$

101. Physical Properties. — Pure nitric acid is a colorless liquid about $1\frac{1}{2}$ times as heavy as water. The nitric acid of commerce usually contains 40 to 60 % of water and a small amount of nitrogen peroxid, which gives to it its color.

102. Chemical Properties. — Nitric acid is the most unstable of the common acids; 76 % of its weight is oxygen, and the ease with which it is decomposed leads to its extensive use as an oxidizing agent. The first steps of the process of making sulfuric acid illustrate this action.

As was shown in Experiment 35, when a metal is dissolved in hydrochloric acid, hydrogen is evolved. When a metal is dissolved in nitric acid, however, no hydrogen is given off, but the result is the same as though hydrogen was first set free and afterward took oxygen from some of the remaining nitric acid, forming water and reducing the acid to one or more of the oxids of nitrogen represented by the following formulæ, N_2O, NO, NO_2, or even to ammonia or nitrogen. The interesting point here is the fact that when hydrogen gas is passed through nitric acid it does not decompose the nitric acid molecule, while in the case under

consideration the hydrogen from the nitric acid molecule does decompose it. Instances of the increased chemical activity of elements which are taking part in certain chemical changes are quite numerous, and the cause of the increased activity is fully discussed in § 179 on the nascent state.

Further chemical properties are illustrated in the following experiments: —

Experiment LII. Nitric Acid as an Oxidizing Agent. — Place a cubic centimetre of powdered charcoal on a piece of sheet iron, apply heat until the charcoal begins to glow. Using a clean glass tube, drop a few drops of concentrated nitric acid on the red hot charcoal. What occurs? Account for the explosion.

Alternate. — Pour a few cubic centimetres of concentrated nitric acid into a test tube. Partly close the open end of the test tube with absorbent cotton, holding the tube with the test-tube holder and over the yellow dish so as to catch the acid in case the tube breaks. Boil the acid.

Describe, and account for the action observed.

Experiment LIII. Nitric Acid as a Solvent. — Test the solubility of the following metals: tin, lead, zinc, copper, iron, gold, and silver in *dilute* nitric acid. If any of the metals fail to dissolve, apply heat. Determine whether hot *concentrated* nitric acid will dissolve any of the metals not acted upon by the hot dilute acid.

Write the reactions.

Note. — The symbol of copper nitrate is $Cu(NO_3)_2$, and those of other nitrates are similar to it.

Experiment LIV. Action of Nitric Acid on Various Substances. — In a medium sized bottle containing dilute nitric acid place a small piece of each on the following substances: white kid, white flannel, white silk, cotton, linen, asbestos, and bleached hemp; stir them occasionally with a glass rod. Describe any change of color observed. Determine whether the color is permanent by endeavoring to wash it out. Which of the substances are dyed? Which are mineral substances? which vegetable? which animal? Inference?

Experiment LV. Etching. — Cover the metal to be etched with melted paraffin; after the wax has cooled sketch the design with a

sharp instrument, taking care to cut through the paraffin. Cover the design with nitric acid, which dissolves the metal where the paraffin has been removed, and thus etches the design on the plate. After a few minutes wash off the acid and remove the paraffin.

103. Uses of Nitric Acid. — Nitric acid is used in etching, dyeing, oxidizing silver, and in the arts; for example, in the manufacture of nitroglycerin, guncotton, sulfuric acid, and as a solvent for silver in the processes of photography.

REVIEW QUESTIONS

1. How are the plates used in printing "etchings" prepared?
2. State the occurrence of nitric acid in nature. Is it ever found uncombined?
3. How does the nitric acid of commerce differ from the chemically pure article?
4. State the properties and uses of nitric acid, and describe its preparation.
5. For what purpose is sulfuric acid used in the manufacture of nitric acid?
6. Account for the unstable character of nitric acid.
7. Why is nitrogen an important constituent of most explosives?

CHAPTER XII

ACIDS

BASES AND SALTS

104. Metallic and Non-metallic Oxids. — It will be remembered that oxygen combines with every element except fluorin, forming oxids. Most of these oxids combine with water to form hydroxids which belong to one of two classes possessing opposite chemical properties, for example, the following oxids form acids when treated with water

Non-metallic Oxids.

Sulfur dioxid, $SO_2 + H_2O = H_2SO_3$, sulfurous acid.
Sulfur trioxid, $SO_3 + H_2O = H_2SO_4$, sulfuric acid.
Carbon dioxid, $CO_2 + H_2O = H_2CO_3$, carbonic acid.
Nitrogen trioxid, $N_2O_3 + H_2O = 2\,HNO_2$, nitrous acid.
Nitrogen pentoxid, $N_2O_5 + H_2O = 2\,HNO_3$, nitric acid.

Those included in the following list are called bases.

Metallic Oxids.

Sodium oxid, $Na_2O + H_2O = 2\,NaHO$, caustic soda.
Potassium oxid, $K_2O + H_2O = 2\,KHO$, caustic potash.
Calcium oxid, $CaO + H_2O = CaH_2O_2$, slaked lime.
Ferric oxid, $Fe_2O_3 + 3\,H_2O = Fe_2H_6O_6$, ferric hydroxid.

The oxids which form these compounds are distinguished as acid-forming oxids and basic oxids. This classification is not complete, as some oxids have neither acid nor basic properties, *e.g.* water, H_2O, nitrous oxid, N_2O, etc.; and

certain oxids act either as acid-forming or basic oxids, depending upon the element with which they combine; but the importance of the two classes, and of the compounds formed when they unite, makes a somewhat extended study of their properties desirable. The metallic elements, or those which form basic oxids, are much more numerous than the non-metallic, or those which form acids, there being only fifteen of the latter.

105. Definitions.

Acid. — *A compound containing one or more atoms of hydrogen which may be displaced by a metal.*

Base. — *A compound containing hydrogen, oxygen, and a metal which may be displaced by the hydrogen of an acid.*

Salt. — *A compound formed when a metal replaces one or more atoms of hydrogen in an acid.*

Salts are sometimes formed by direct union of an acid-forming oxid and a basic oxid, in which case the salt is the only product of the action; when an acid combines with a base, however, the acid liberates hydrogen, taking the metal of the base and forming a salt; and the liberated hydrogen of the acid with the hydrogen and oxygen of the base form water.

106. Characteristics of the Stronger Acids.

Acids have a strong affinity for all bases.

They are all soluble in water.

They have a sour taste.

They turn vegetable blues red.

They decompose carbonates.

They combine with alkalies, losing their own properties and destroying those of alkalies.

The only element common to all acids is hydrogen. Nearly all acids contain both hydrogen and oxygen, but a

few are binary. The most notable of these are formed by the union of hydrogen with some member of the chlorin family, but there are some others, such as the compound of hydrogen and sulfur, sometimes called hydrosulfuric acid, and the compound of hydrogen and nitrogen known as hydrazoic acid.

107. Rules for Naming Acids. — The terminations "ous" and "ic" are applied to acids, and indicate the amount of oxygen in the compound, just as they do when applied to oxids: thus HNO_3 is nitric acid, and HNO_2 is nitrous acid.

All the binary acids end in "ic," and have the prefix "hydro." The prefix "per" indicates more oxygen than the "ic" acid, and the prefix "hypo" less oxygen than the "ous" acid, *e.g.*: —

HCl, Hydrochloric acid
$HClO$, Hypochlorous acid
$HClO_2$, Chlorous acid
$HClO_3$, Chloric acid
$HClO_4$, Perchloric acid

108. Characteristics of the Bases. — The properties of the bases are in a general way opposite to those of acids. They restore colors reddened by acids, and turn vegetable colors blue.

109. Rules for Naming Salts. — The name of the salt formed when a given acid combines with a base, consists of two parts.

First Part. — The name of the metal replacing the hydrogen of the acid.

Second Part. — The name of the acid modified in accordance with the following rules: —

RULE I. — *Names of acids containing oxygen, ending in "ic," have the termination changed to "ate," e.g.:* —

Nitric acid forms nitrates.
Acetic acid forms acetates.
Sulfuric acid forms sulfates.

RULE II. — *Names of acids containing oxygen, ending in "ous," have their termination changed to "ite," e.g.:* —

Nitrous acid forms nitrites.
Chlorous acid forms chlorites.
Sulfurous acid forms sulfites.

RULE III. — *The prefix "hydro" is dropped from the name of the binary acids, and the termination "ic" is changed to "id," e.g.:* —

Hydrochloric acid forms chlorids.
Hydrocyanic acid forms cyanids.
Hydrofluoric acid forms fluorids.

REVIEW QUESTIONS

1. Write the names of the salts formed by the union of the following bases with hydrochloric, nitric, sulfuric, chlorous, nitrous, hydrocyanic, sulfurous, and chloric acids: —

Sodium hydroxid, NaHO
Potassium hydroxid, KHO
Calcium hydroxid, CaHO

2. Write the names of the salts formed by the action of each of the above acids on the following basic oxids: —

Lead oxid, PbO
Copper oxid, CuO
Silver oxid, AgO

3. Define and illustrate acid, salt, base.
4. State how a binary compound is named. Illustrate.
5. State and illustrate the meaning of hypo, per, id (ide), ate, ous.
6. State and illustrate five principles of chemical nomenclature.
7. State the characteristics of the stronger acids.

CHAPTER XIII

COMPOUNDS OF NITROGEN AND OXYGEN

110. Nitrogen combines with oxygen to form five distinct compounds having the following compositions: —

Nitrogen monoxid,	N_2O
Nitrogen dioxid,	N_2O_2 or NO
Nitrogen trioxid,	N_2O_3
Nitrogen tetroxid,	N_2O_4 or NO_2
Nitrogen pentoxid,	N_2O_5

111. **Nitrogen Monoxid** was formerly called nitrous oxid. It is also known as laughing gas. It does not occur in nature.

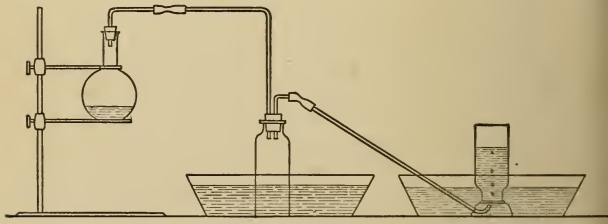


FIG. 12.

(*a*) *Preparation.*

Experiment LVI. (Two students work together.) — 1. Place 15 grammes ammonium nitrate (NH_4NO_3) in a flask. Connect this with a dry bottle placed in a dish of water; from this bottle lead the gas to the water pan, as shown in the sketch. Heat the flask very gradually; if too high a temperature is reached, nitric oxid may be formed and an explosion may occur.

2. Collect five bottles of the gas. The first bottle will be mixed with air; throw it away. Do not allow all of the ammonium nitrate to boil away.

3. Test the second bottle with a glowing splinter. Does the gas support combustion?

4. Remembering that combustion is a union with oxygen, answer the following questions: —

Is the nitrous oxid decomposed? Does nitrous oxid cause a glowing splinter to burst into flames? Note the color, odor, taste of the gas.

5. Remove the third bottle from the pan when about $\frac{1}{2}$ full of gas. Cover the mouth of the bottle with the hand and shake vigorously. Is a vacuum formed? Is the gas soluble?

6. Lower a small piece of burning phosphorus into the fourth bottle. What occurs? Ignite a small amount of sulfur with a match and lower it into the fifth bottle. Does it burn? If not, use a Bunsen burner to ignite the sulfur, and see that it is burning vigorously before you test the gas. Explain the action.

7. Examine the condensing bottle, and so state the source of the liquid it contains. Has it an odor or a taste? Compare the taste with that of ammonium nitrate. Has any of the ammonium nitrate been carried over into the condensing bottle without chemical change?

Reaction: $NH_4NO_3 = N_2O + 2\ H_2O$.

(*b*) *Properties.*

In addition to the properties already shown nitrogen monoxid possesses the following characteristic properties: —

When inhaled it produces a kind of intoxication usually manifested by hysterical laughing; hence its name. If more of the gas is inhaled, this is followed by unconsciousness, lasting a few minutes. It is well adapted to use as an anæsthetic in minor surgical operations, but special care must be taken that the gas used for this purpose be pure; if made from ammonium nitrate, containing ammonium chlorid, the gas always contains chlorin; if heated too strongly, ammonium nitrate yields nitric oxid and possibly hyponitrous acid. If either of these is present, the gas is unfit to breathe. It may be freed from these substances, however, by agitation with ferrous sulfate solution.

When liquid nitrogen monoxid is evaporated in a vacuum with carbon disulfid, it produces the remarkably low temperature — 140° C.

Water at 0° C. dissolves a little more than one volume of the gas.

When slightly heated in an atmosphere of this gas metallic potassium and sodium burn brightly, forming oxids; if strongly heated, nitrates are formed.

112. Unstable Characteristics of Nitrogen Monoxid and Ammonium Nitrate. — In Experiment 56 the feeble affinity which binds the elements of ammonium nitrate together was illustrated. At ordinary temperatures it is a stable compound, but at a temperature somewhat above its melting point the compound is decomposed, forming nitrous oxid and water as indicated in the equation on page 85. If the temperature is too high, nitric oxid and water are formed, leaving one-half of the nitrogen in the free state.

$$NH_4NO_3 = 2\,H_2O + NO + N_2.$$

The so-called ability of nitrous oxid to support combustion is due to and is an illustration of its unstable character. In all cases it is the oxygen of the nitrous oxid which supports combustion, and the phenomenon is preceded by the decomposition of the gas.

113. Nitrogen Dioxid was formerly called nitric oxid. Its molecular formula is believed to be NO instead of N_2O_2, because its density is 15, and if the latter formula was chosen it would be an exception to the rule that the density of any compound gas is half its molecular weight. It does not occur in nature.

(*a*) *Preparation.*

Experiment LVII. (Performed only under hood.) — Place a small handful of copper clippings in a generating bottle, and arrange appa-

ratus as for the preparation of hydrogen, Experiment 35. Pour about 50 cc. of water into the generating bottle, and add an equal quantity of nitric acid.

Look for evidence of the formation of a colored gas, a colorless gas, a soluble gas.

Collect six bottles of the gas, pour the liquid of the generating bottle into the copper nitrate bottle, rinse the copper which remains in the bottle with plenty of water, and put it away to be used again. Note the color of the gas collected, the color of the liquid in the generating bottle.

1. Remove the cover of the first bottle. Do you note any change in color? Is it possible that this bottle contains air only?

2. Allow the gas in the second bottle to escape into the air. What change of color occurs? Which of the elements in the air is most active, and therefore most likely to be the cause of the change? Does the colored gas formed resemble that formed in the generating bottle at first? How do you account for this? Does the colored gas seem heavier, or lighter than air? If the colored gas is formed by oxidation of the colorless gas, how should their densities compare?

3. Hold the third bottle in a horizontal position, and while in this position remove the glass plate which covers it. Notice whether air diffuses into the upper or the lower part of the bottle. What does this show as to the relative weight of air and nitric acid?

4. Lower a lighted candle into the fourth bottle. Result? Ignite some sulfur in an ignition spoon, and when it is burning vigorously lower it into the same bottle. Result? Remove all traces of sulfur from the ignition spoon, cool it with water, dry it, and place a small piece of dry phosphorus in it. Ignite the phosphorus by touching it with a hot wire, and quickly lower it into the fourth bottle. Result?

5. Ignite a piece of phosphorus, and when it is burning actively lower it into the fifth bottle. Result? Nitric oxid contains a larger percentage of oxygen than nitrous oxid. In the light of this fact how can you explain the difference in the behavior of the two gases?

6. Pour a few drops of carbon disulfid into the sixth bottle; after a few minutes apply a lighted match. Describe the result. What is deposited on the sides of the bottle?

Reaction. — The reaction may be considered as taking place in two stages. First,

$$Cu + 2\,HNO_3 = Cu(NO_3)_2 + 2\,H.$$

The hydrogen, however, does not appear as a gas, but passes

directly from the nitric acid molecule, from which it has been displaced, into combination with the hydrogen and oxygen of other molecules of nitric acid, as shown by the equation,

$$6\,H + 2\,HNO_3 = 4\,H_2O + 2\,NO.$$

Complete the following reaction, which expresses both of the above changes: —

$$3\,Cu + 8\,HNO_3 = 3\,Cu(NO_3)_2 + ?NO + ?H_2O.$$

The hydrogen is said to be in the nascent state; see § 179.

(*b*) *Properties.*

When strongly heated, metallic potassium decomposes nitric oxid and burns brightly, but metallic sodium remains unchanged. It is not easily condensed to a liquid, requiring a pressure of more than a hundred atmospheres at a temperature of 11° C. Its most important chemical property was illustrated by its behavior in air.

114. Nitrogen Tetroxid or Nitrogen Peroxid, NO_2. — The reddish brown gas noticed in Experiment 57 is nitrogen peroxid. It has a disagreeable odor and is poisonous. It is heavier than air (it is warm when first formed and rises) and is very soluble in water. At 9° C. it solidifies to colorless crystals. The bonds which hold the oxygen to the nitrogen in this compound are not nearly so strong as in nitric oxid, and upon this fact depends its value as an oxidizing agent, as illustrated in the process of manufacturing sulfuric acid. Metallic potassium bursts into flame in this gas.

115. Nitric Oxid and Nitrogen Peroxid as Reducing and Oxidizing Agents. — In nitric oxid the oxygen is held rather firmly by the nitrogen, and there seems to be a demand for more oxygen. The action of this substance as a reducing agent depends upon its ability to take oxygen from other substances (a limited number) as illustrated by the formation of nitrogen peroxid in Experiment 57.

When the additional atom is obtained, the compound is held together by a very feeble affinity, and nitrogen peroxid is an excellent oxidizing agent; it gives up its oxygen to substances having but little affinity for it.

REVIEW QUESTIONS

1. State the physical properties of nitric oxid: (*a*) color, (*b*) weight, (*c*) odor, (*d*) solubility, (*e*) liquefaction.

2. Compare the chemical properties of nitrogen monoxid with those of the dioxid.

3. Is there any evidence that the oxygen is held with stronger bonds in nitrogen dioxid than in the monoxid?

4. Arrange phosphorus, sulfur, and nitrogen in the order of their affinity for oxygen as shown in Experiment 58.

5. What chemical property enables us to distinguish oxygen from nitrogen monoxid?

6. What physical property enables us to distinguish oxygen from nitrogen monoxid?

7. Discuss the physical properties of nitrous oxid as follows: —

(*a*) taste, (*b*) odor, (*c*) color, (*d*) weight, (*e*) solubility.

8. Distinguish between oxygen and nitrous oxid with respect to (*a*) taste, (*b*) solubility, (*c*) chemical energy, (*d*) affinity for sulfur. What chemical properties has nitrous oxid?

9. State the chemical and physical properties of nitrogen tetroxid.

10. Describe an experiment illustrating the unstable character of nitrogen compounds.

11. Describe an experiment illustrating the unstable character of ammonium nitrate.

12. Describe the ordinary preparation of nitrous oxid and name the property of nitrogen which makes this preparation easy.

13. Describe an experiment to show the unstable character of nitrogen monoxid.

14. Name five binary compounds of nitrogen and oxygen, and after each name write its formula. What law is illustrated by these compounds?

15. Define oxidizing agent; reducing agent. What compound of nitrogen is used in oxidation? reduction? Why?

16. Explain the difference in the behavior of potassium when slowly heated in atmospheres of nitrous oxid, nitric oxid, and nitrogen peroxid.

CHAPTER XIV

THE CHLORIN FAMILY

116. The elements fluorin, chlorin, bromin, and iodin resemble each other in chemical affinities and other properties, and are, therefore, treated as members of the same family. They are sometimes called the halogens.

SECTION I. — CHLORIN

SYMBOL Cl. — ATOMIC WEIGHT 35.5

117. Occurrence. — Chlorin does not occur free in nature, but its compounds are widely distributed and very abundant. Common salt, which is present in large quantities in sea-water, is sodium chlorid, NaCl; sea-water also contains chlorids of magnesium and potassium. Horn silver, one of the most important ores, is silver chlorid, AgCl; and all plants contain the chlorids of potassium and sodium.

118. Preparation. — (*a*) *First Method. From Bleaching Powder.* (*Chlorid of Lime.*) (To be performed only under the hood.)

Experiment LVIII. — Place 15 grammes of bleaching powder in a flask, and pour through a funnel tube about 30 cc. of dilute sulfuric acid. Collect the gas by displacement of air.

In the arts this process is extensively used. Paper rags are boiled in alkali to remove the grease, then placed in a large vat with bleaching powder and sulfuric acid; when

they come out they are a pure white. Cotton cloth is bleached by passing it through alternate vats of sulfuric acid and chlorid of lime.

(*b*) *Second Method. From Hydrochloric Acid.*

Experiment LVIX. (Performed by the instructor.) — Mix 12 grammes manganese dioxid, MnO_2, and enough hydrochloric acid, HCl, to cover it, in a flask, and gradually apply heat. Collect three bottles of gas by downward displacement of air, as shown in sketch. Now substitute for the dry bottle a bottle nearly full of water, and allow the gas to bubble through it for a time. Note the color, odor, solubility, and weight of the gas.

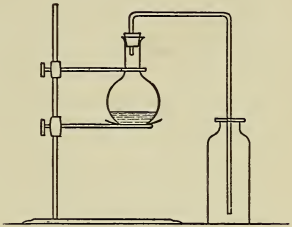


Fig. 13.

Reaction : $MNO_2 + 4\,HCl = 2\,H_2O + 2\,Cl + MnCl_2$.

Experiment LX. Affinity of Chlorin for Metals. — Throw a small amount of powdered antimony into a jar of chlorin. What occurs? Is this combustion ?

Experiment LXI. Affinity of Chlorin for Hydrogen. — 1. Prepare hydrogen as directed in Experiment 35. When the gas is pure, fit the generating bottle with a jet, as shown in this figure ; light the hydrogen, and introduce the jet into the second jar of chlorin. Does the hydrogen burn ? Is there any change in the color of the flame ? in the color of the contents of the jar ? Hold a piece of moist blue litmus paper in the jar. What new substance is present ?

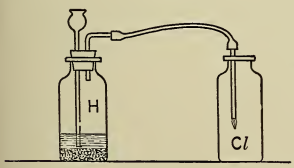


Fig. 14.

2. Introduce a burning candle into the third bottle of chlorin, and note what takes place. State any explanation of the difference in the

results obtained in this experiment and in the preceding one that occurs to you.

3. Moisten a bit of tissue paper with warm turpentine and drop it into the fourth bottle of the chlorin. What occurs?

Turpentine is composed of carbon and hydrogen. In the above experiment the hydrogen is taken by the chlorin, and the carbon is liberated as "smoke."

If chlorin water is exposed to sunlight long enough (say several days), it is found that oxygen is set free, the chlorin having taken the hydrogen from the water, leaving the oxygen. If any substance that has an affinity for oxygen is present in the water, the chlorin acts more rapidly.

Experiment LXII. Affinity for Hydrogen. Bleaching. — 1. In the fifth bottle of chlorin place a moistened rose. What occurs?

2. In another bottle drop a piece of moist, colored calico.

3. Write your name in ink, and pour some of the chlorin water made in Experiment 60 over it.

4. Try the effect of chlorin water on printers' ink. All except one of the coloring matters tested are attacked by oxygen in the nascent state. Which one was not?

In bleaching, the chlorin may sometimes act directly on the coloring matter, but very frequently its action is due to its tendency to take hydrogen from water, thus making it easier for other substances to obtain oxygen. Chlorin is, therefore, often called an oxidizing agent. Its action as a disinfectant is somewhat similar to its action as a bleaching agent.

119. Physical Properties. — Chlorin is $2\frac{1}{2}$ times heavier than the air. One litre weighs 3.167 grammes. One volume of water will dissolve two volumes of chlorin. The name chlorin is derived from the Greek word meaning green.

At ordinary pressures chlorin may be liquefied at $-34°$ C.; a pressure of six atmospheres is required at 0° C.

120. Chemical Properties. — Chlorin combines with most substances at ordinary temperatures, and is remarkably active. It has a marked affinity for hydrogen and for metals, as is shown by the large number of chlorids known. If inhaled in concentrated form, death will result. It combines with hydrogen with explosive violence when the mixture is heated, or even exposed to the sunlight.

121. Uses. Bleaching. — Chlorin is extensively used in the arts as a bleaching agent. It destroys the molecules of vegetable coloring matter by replacing its hydrogen, or by adding oxygen. Moist articles bleach very rapidly because the water is decomposed by the chlorin, and nascent oxygen assists in the destruction of the coloring matter.

Disinfection. — Chlorin is one of the best disinfectants we have. It is this substance that our health officers depend upon to keep cholera out of the country. Liquid chlorin is now an article of commerce, and large quantities are sold in iron cylinders for use in certain processes of extracting gold from its ores, and other chemical processes requiring the gas.

SECTION II. — HYDROCHLORIC ACID

SYMBOL HCl. — MOLECULAR WEIGHT 36.5

122. Occurrence. — This gas is not found free in nature except in the gases evolved from certain active volcanoes; its salts, the chlorids, are abundant and important, as was stated in the last chapter, and from one of these, viz. sodium chlorid, or common salt, nearly all the hydrochloric acid of commerce is obtained.

123. Preparation. (*a*) *By Synthesis.* — If equal volumes of hydrogen and chlorin be mixed in a flask and exposed to the sun, an explosion takes place, and hydrochloric acid is

formed. This illustrates the fact that light sometimes aids chemical action.

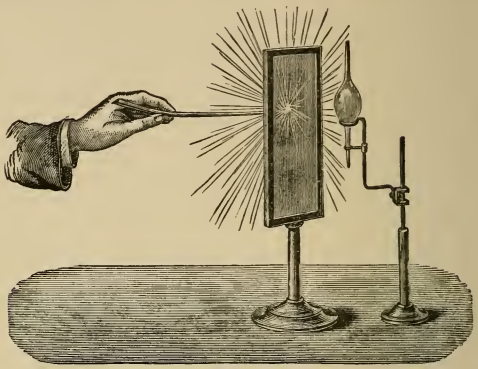


Fig. 15.

Caution. — The explosion sometimes breaks the flask, and to protect the experimenter from injury a screen of plate glass is usually placed in front of it. If a thin-walled flask be used, there is little danger of the flying fragments breaking the screen.

(*b*) *By Burning Hydrogen in Chlorin.*

Hydrochloric acid was prepared synthetically in Experiment 60, which see.

(*c*) *By the Action of Sulfuric Acid on Common Salt.*

Experiment LXIII. — Arrange the apparatus as in Experiment 50. With 20 cc. of water in the first bottle, and about 50 cc. in each of the others, place 10 grammes common salt in a flask, and when your apparatus is all ready, and you are sure that all joints are tight, pour into the flask 17 cc. of sulfuric acid diluted with 10 cc. of water. Gas is immediately evolved. Heat gradually. Test the gas as follows: —

1. Hold moist litmus paper in a stream of the gas. Note effect. Is the gas visible in the air?

2. Prove the solubility of the gas. Is the gas in the flask visible?

3. Does hydrochloric acid burn? Does it support combustion?

4. Pour a few drops of the liquid in the first bottle into about a tablespoonful of water, and taste.

5. Describe the odor.

6. Drop a piece of zinc in the first bottle. What occurs? Is hydrogen given off?

Caution. — The tube which connects the flask with the first bottle should not dip beneath the water. In the other bottles the tube by which the gas enters should enter the water. Watch the apparatus carefully, and prevent the water from running from one bottle into another, by raising the stopper of the bottle toward which it is running.

124. Reactions. — When prepared as above, hydrogen sodium sulfate is formed with the following results: —

Reaction: $NaCl + H_2SO_4 = HCl + HNaSO_4$.

If concentrated sulfuric acid be used with an excess of salt and a higher temperature maintained, the same weight of sulfuric acid will form twice as much hydrochloric acid, and the by-product is the normal sodium sulfate instead of the hydrogen sodium sulfate.

$$2\,NaCl + H_2SO_4 = 2\,HCl + Na_2SO.$$

125. Properties. — Experiment 63 taught us the color, odor, solubility, combustibility, and acid reaction of hydrochloric acid gas, and illustrated the use of its aqueous solution as a solvent. The dry gas is transparent, but in contact with moist air a dense cloud is formed by the solution of the gas in an aqueous vapor. At 0° C., water dissolves five hundred times its own volume of hydrochloric acid. As the temperature rises, the solubility diminishes, so that at 50° C. only 364 volumes will be dissolved. The pure gas dissolved in pure water is colorless; the commercial acid, a solution containing about 30% of the gas, owes its yellow color to the presence of a small quantity of iron.

Hydrochloric acid gas may be liquefied at 10° C. by a pressure of forty atmospheres; the liquid obtained is colorless, and is almost without action on metals. The aqueous solution of the gas dissolves iron, zinc, and many other metals, forming chemical solutions, but it is not as valuable a solvent as nitric acid, which was formerly called "Aqua Fortis," or strong water, because of its ability to dissolve so many substances. The mixture of nitric and hydrochloric acids known as "Aqua Regia," or royal water, is a better solvent than either of its components. This name was given to it by the alchemists because it dissolves gold, which they considered the king of metals; it also dissolves platinum and certain ores, forming chlorids of the metals. Its action is due to the nascent chlorin evolved when the acids are mixed.

126. Composition of Hydrochloric Acid. — It has been shown that one volume of hydrogen and one volume of chlorin combine to form two volumes of hydrochloric acid; and since the atomic weight of chlorin is 35.5, it follows that 36.5 parts by weight of hydrochloric acid will contain 35.5 parts of chlorin and one part of hydrogen.

127. The Manufacture of Hydrochloric Acid. — Large quantities of hydrochloric acid are now obtained as one of the by-products in the Leblanc process of manufacturing soda-ash. In the first stage of this process salt is treated with sulfuric acid, and heated to convert it into sodium sulfate: the hydrochloric acid gas was formerly allowed to escape into the atmosphere. The acid-laden atmosphere destroyed all vegetable life in the vicinity of the alkali works; farms were rendered worthless, the limestone and metal work of buildings was attacked and destroyed, and the death

rate increased. In England the nuisance led to the "Alkali Act," which compelled all manufacturers to absorb the hydrochloric acid. This is now accomplished by passing through tall brick-lined chimneys loosely filled with coke or bricks, and at the top of which a spray of water is introduced. The water at the bottom of the chimney is nearly saturated with the gas. The commercial acid thus prepared is now an important source of income to the manufacturer.

128. Uses. — Hydrochloric acid is extensively used in the preparation of ammonium chlorid, and of bleaching powder, and is an important reagent in the laboratory.

SECTION III. — OTHER COMPOUNDS OF CHLORIN

129. Oxids. — By indirect methods two compounds of chlorin and oxygen may be obtained, having the formulas Cl_2O and ClO_2; they are very unstable compounds, and are, therefore, powerful oxidizing agents, but are of little importance.

130. Acids. — Three acids containing hydrogen, chlorin, and oxygen are known: —

Hypochlorous acid,	$HClO$
Chloric acid,	$HClO_3$
Perchloric acid,	$HClO_4$

These acids are also very unstable, and are good oxidizing agents; they are chiefly important because of the importance of their salts, which will be discussed later.

131. Preparation of the Acids. — If a perchlorate is treated with strong sulfuric acid, a sulfate is formed, and perchloric acid may be obtained from the solution by distillation.

When a solution of a chlorate is treated with sulfuric acid, chloric acid is liberated, but it cannot be separated from the solution by distillation, because decomposition takes place. If barium chlorate be used, the sulfate formed is precipitated and chloric acid is left in solution.

Hypochlorous acid cannot be obtained in this way, because it is decomposed by the stronger acids with the liberation of chlorin. It is probable that hypochlorous acid is formed, but is at once decomposed by the sulfuric acid.

132. Formation of Sodium Chlorid by the Action of Hydrochloric Acid on Baking Soda. — If hydrogen sodium carbonate (baking soda) is treated with hydrochloric acid, carbon dioxid, CO_2, is given off and common salt is formed.

$$HCl + HNaCO_3 = NaCl + H_2O + CO_2.$$

This reaction is very similar to that which occurs when baking powder is moistened, the only difference being that rochelle salt is formed by the baking powder instead of common salt. It has been suggested that, inasmuch as rochelle salt is an injurious ingredient in food, and as common salt is commonly used, it would be an improvement on existing methods of preparing biscuit, if baking soda and hydrochloric acid should be used instead of baking powder. There are practical difficulties, however, in determining the exact amount of hydrochloric acid to use, and the mistakes which would follow its general use would doubtless cause serious illnesses.

SECTION IV. — BROMIN

SYMBOL BR. — ATOMIC WEIGHT 80

133. Occurrence. — Bromin does not occur free in nature, but its compounds, the bromids, are found in small quantities

in sea-water and in the waters of certain salt wells and mineral springs. After the extraction of the common salt from sea-water, there remains a heavy yellow liquid called bittern, which contains sodium and magnesium bromids; this was formerly the principal source from which the bromin was obtained, but the bromids are found in larger quantities in the upper layers of certain salt deposits, and bromin can therefore be prepared more economically from these layers than from bittern.

134. Preparation. — Bromin is prepared by distilling a bromid with manganese dioxid and sulfuric acid and condensing the vapor evolved in a well-cooled receiver. It may also be prepared by treating a bromid with chlorin. The stronger chemical affinity of the chlorin for the metal enables the chlorin to decompose the bromid, forming a chlorid and setting the bromin free.

Experiment LXIV. — 1. Examine liquid bromin while contained in a bottle; note its color and odor. (Care.) Is it a mobile or a viscous liquid? How do you think its density compares with that of water? Pour a few drops into a test tube containing water. Does the bromin float on the water or sink? Does it dissolve in water? Is bromin as soluble as chlorin?

2. To one or two cubic centimeters of carbon disulfid in a test tube, add a few drops of the water to which bromin was added. What color is obtained? This is the test for free bromin.

135. Physical Properties. — Bromin is the only non-metallic element that is a liquid at ordinary temperatures. It is volatile and very poisonous, and its vapor is more than five times as heavy as air.

136. Chemical Properties. — Bromin closely resembles chlorin in its chemical affinities. It combines directly with metals and has a strong affinity for hydrogen.

137. Uses. — The ease with which it abstracts hydrogen from substances leads to its use as a disinfectant and to a limited extent as a decolorizer. Its compounds are used in medicine and in photography.

138. Test. — When bromin is dissolved in carbon disulfid, an orange liquid is obtained which is characteristic. It also turns starch a bright yellow color.

139. Hydrobromic Acid, HBr. — This acid corresponds to hydrochloric acid, which it resembles in its chemical properties as well as in composition.

SECTION V. — IODIN

SYMBOL I. — ATOMIC WEIGHT 127

140. Occurrence — Like other halogens, iodin occurs in nature only in combination. It is found in sea-water, in the waters of many mineral springs, and in several important minerals, but the quantity of iodin present in each case is exceedingly small. Certain sea-weeds absorb it from sea-water, and much of the iodin of commerce is obtained from this source, but the dried weeds contain less than one-half of 1 % of iodin. The crude sodium nitrate, known as Chili saltpetre, contains about 0.2 % of iodin, chiefly as sodium iodate. For a number of years the amount of iodin obtained from this source exceeded the total consumption of the whole world.

141. Preparation. — Iodin may be prepared by distilling a salt containing it with manganese dioxid and sulfuric acid, and condensing the vapor in a cooled receiver. A solution containing an iodin salt may be obtained by leaching the ashes of sea-weeds, technically known as *kelp;* or more economically by boiling the sea-weeds with sodium

carbonate and filtering. The liquid thus obtained contains besides the iodin a number of useful substances, which are removed by precipitation or crystallization, the iodin salts remaining in solution. The solutions obtained by these processes are distilled as described above.

142. Physical Properties.

Experiment LXV. — 1. Examine iodin crystals, note the color, lustre, and general form of the crystals.

2. Drop a few crystals on a piece of hot sheet iron, holding the iron under the hood.[1] Note the color of the vapor.

3. Drop a crystal of iodin into a test tube containing water. Does it dissolve? Of the three elements chlorin, iodin, and bromin, which is most soluble in water? which least soluble? which has the greatest atomic weight? which least?

4. Drop the smallest particle of iodin that you can pick up on a knife blade into a test tube containing carbon disulfid. Note the color of the solution. This is often used as a test for free iodin.

Iodin sublimes slowly at ordinary temperatures, condensing on the side of the bottle containing it which is away from the light. At 107° C. it melts, giving off the heaviest known vapor.

143. Chemical Properties. — The chemical affinities of iodin are similar to those of chlorin and bromin, but are less energetic.

Starch is turned a dark blue by iodin.

Experiment LXVI. Relative Affinity of Chlorin, Iodin, and Bromin for Metals. — 1. Pour about 1 cc. of a solution of potassium bromid into a test tube containing an equal amount of carbon disulfid; shake the tube. Does bromin in combination change the color of the carbon disulfid? Add a little chlorin water to the mixture, and shake the tube to mix the liquids thoroughly. Is there any evidence of free chlorin now? Which has the stronger affinity for potassium, bromin or chlorin?

[1] In laboratories not provided with a hood, it is suggested that the teacher perform this experiment, dropping the iodin into a flask and heating it

2. Using a solution of potassium iodid instead of potassium bromid, repeat the experiment. Does iodin in combination change the color of carbon disulfid? Does chlorin water set iodin free? Which has the stronger affinity for potassium, iodin or chlorin?

3. Pour some bromin water into a solution of potassium iodid containing some carbon disulfid. Does bromin water set iodin free? Which has the stronger affinity for potassium? Arrange the three elements tested in the order of their affinities for potassium. Also arrange them in the order of their atomic weight. Are the lists the same?

144. Uses. — Dissolved in alcohol it is used in medicine as tincture of iodin. Its compounds are used in photography and the manufacture of aniline.

145. Hydriodic Acid, HI. — Corresponds to hydrochloric acid.

SECTION VI. — FLUORIN

SYMBOL F. — ATOMIC WEIGHT 19

146. Occurrence. — This remarkable element does not occur free in nature, and until recently has resisted all attempts to isolate it. Its compounds have long been known. Fluorspar, the cubical purple crystal occurring in the Niagara limestone at Rochester, N.Y., and elsewhere, is calcium fluorid, CaF_2, and cryolite is a double fluorid of sodium and aluminum. Fluorin also occurs in the teeth, bones, and blood of animals.

147. Preparation. — Fluorin cannot be prepared by the method employed in preparing the other members of this family, because of its intense chemical energy. Its compounds are not easily decomposed, and when the chemist succeeds in decomposing one of them the liberated fluorin usually forms a new compound with some element. It has, in many experiments, combined with the material of the vessel in which it was separated. Gold, platinum, glass, and

carbon vessels have been tried, but in each case a fluorid was obtained instead of the element. In 1886, Moissan solved the problem by electrolyzing a solution of the acid potassium fluorid in anhydrous hydrofluoric acid in a U-tube made of an alloy of platinum and iridium.

148. Physical Properties. — Fluorin is a pale yellow-green gas about $1\frac{1}{4}$ times heavier than air. Its odor is not definitely known, as it attacks the mucous membranes. Its solubility in water is unknown, for it decomposes water, forming hydrofluoric acid, HF.

149. Chemical Properties. — Fluorin combines with metals, heat and light being developed in some cases; in contact with hydrogen it at once explodes; iodin, sulfur, and phosphorus melt and burst into flame in fluorin; silicon takes fire and burns with great brilliancy, and organic compounds are quickly destroyed in the gas.

150. Hydrofluoric Acid, HF. — This powerful acid is a colorless, fuming liquid which must be handled with the greatest care. Inhaled in a pure state, it causes death, and even when greatly diluted with air, irritates the respiratory organs. A single drop on the skin produces ulcerated sores, accompanied by aching pains throughout the whole body. It has a strong affinity for water, and mixed with it has the power of dissolving glass. The dry gas does not attack glass, the slightest trace of moisture being necessary. The commercial acid is a solution in water, and is largely used for etching designs on glass and for etching the graduations upon measuring glasses, thermometers, etc. It must be kept in gutta percha or wax bottles. The hydrofluoric acid of commerce is prepared by distilling fluorspar and sulfuric acid in leaden retorts and dissolving the vapor in water contained in a series of leaden bottles.

151. Process of Etching Glass.

Experiment LXVII. — Let each student provide himself with a glass slip such as is used for microscope slides.

1. Coat the glass with wax by dipping it in a dish containing melted beeswax (not too hot), and holding it horizontally while the wax cools.

2. Write on the slip with a hat pin, being careful to cut through the wax. The instructor will place a leaden tray under the hood and pour into it a small amount of commercial hydrofluoric acid and an equal quantity of water.

3. Place the slip in the tray, engraved side downward; allow it to remain five minutes. Remove the slip with a pair of crucible tongs, dropping it into a basin of water.

4. Remove the wax with a knife and wash the slip with benzine. If a large piece of glass is to be etched, the following process is preferred. It is quite easy by the following process to etch a large pane of glass with some appropriate design which provides places for the autograph of the members of the class.

Experiment LXVIII. Alternate. — 1. Apply a coat of asphaltum varnish to the article to be etched. When dry, hold it to the light and touch up any air bubbles.

2. Draw the desired design on paper, sprinkle the asphaltum rather thickly with minium, fasten the corners of the design securely to the glass with mucilage. Trace the design with a stylus, using slight pressure; this will cause the minium to adhere to the asphaltum where the stylus has pressed it, and on removing the paper and dusting off the minium the design will be found on the asphaltum in red lines.

3. Cut each line through the asphaltum, using a stylus or a hat pin.

4. Pour strong hydrofluoric acid on the design, allowing it to remain for several minutes. Wash the glass with water and remove the asphaltum with turpentine.

The glass is dissolved by the hydrofluoric acid, and a deep line will be cut wherever the asphaltum has been removed. If the glass has the formula $CaSiO_3$, the reaction is as follows: —

$$CaSiO_3 + 6\,HF = CaF_2 + SiF_4 + 3\,H_2O.$$

152. Properties of the Elements of the Chlorin Family. — The compounds of the members of this family resemble each other in the shape of their crystals, in their chemical properties, and in their composition. The properties of the elements seem to depend upon their atomic weight as shown by the following table: —

	Atomic Weight	State	Color of Vapor	Chemical Activity	Solubility
Fluorin	19	Gas	Almost colorless	—	—
Chlorin	35.5	Gas	Green-yellow	—	—
Bromin	80	Liquid	Red-brown	—	—
Iodin	127	Solid	Violet	—	—

It will be observed that as the atomic weight increases, the density and depth of color of the vapor increase. Fill the blank spaces in the two right-hand columns.

REVIEW QUESTIONS

1. Describe the process and state the theory of bleaching with chlorin.

2. From what is chlorin chiefly obtainable? What property of chlorin renders it valuable in the arts?

3. Describe the preparation of chlorin from hydrochloric acid.

4. If chlorin and hydrogen are mixed and exposed to sunlight, what takes place? What is the product called? What proportions, by volume, of chlorin and hydrogen enter into it? What proportions by weight?

5. Describe two methods of preparing chlorin. Describe an experiment illustrating the affinity of chlorin for metals.

6. Tell what you can of hydrochloric acid as to its manufacture, properties, and uses.

7. In what important acid is chlorin an element? How does this acid affect many of the metals?

8. Describe the formation of sodium chlorid by the action of hydrochloric acid on baking soda.

9. What is aqua regia?

10. How did you prove that hydrochloric acid gas was soluble in water?

11. State the occurrence, properties of fluorin.

12. What difficulties prevent its easy preparation?

13. State the properties of hydrofluoric acid.

14. Describe a process of etching glass.

15. Judging from its atomic weight, how would you expect the chemical activity of fluorin to compare with that of the other halogens?

16. How should its solubility in water compare with the others?

17. Discuss the physical properties of chlorin as follows: (*a*) color, (*b*) odor, (*c*) weight.

18. Discuss chemical properties of chlorin as follows: (*a*) chemical energy, (*b*) special affinities, (*c*) relation to combustion, (*d*) affinities for hydrogen and carbon.

19. Describe the effect of iodin on the skin.

CHAPTER XV

SULFUR AND ITS COMPOUNDS

SECTION I. — SULFUR

SYMBOL S. — ATOMIC WEIGHT 32

153. Occurrence. — In the free state, sulfur is found chiefly in volcanic districts. In this country important deposits are found in California, and in the lava-covered regions of the eastern slope of the Rocky Mountains, particularly in Humboldt County, Nevada. There are also large deposits in Italy, Sicily, Iceland, China, and India. Combined with hydrogen, it occurs in many springs. In combination with metals as sulfids and sulfates, it occurs in enormous quantities in all parts of the world. Many important ores are sulfids, for example, galena or lead sulfid; cinnabar or mercury sulfid; zinc blends or zinc sulfid; realgar or arsenic sulfid, etc. Gypsum and heavy spar are sulfates.

154. Extraction of Sulfur from its Ores. — Native sulfur is usually mixed with earthy or mineral substances, from which it is separated by igniting a part of the sulfur in a limited supply of air; the heat of the burning sulfur melts the rest of the sulfur which is drawn off. In the larger establishments this is conducted in brick kilns with sloping bottoms, in which the melted sulfur is collected. Sometimes the ore is piled up and covered with earth to exclude the air, and the pile is ignited, and the sulfur settles to the

bottom of the pile and runs out through channels dug in the ground. This method is extremely wasteful. Large quantities of sulfur are now obtained as by-products in the process of smelting copper pyrites, of making illuminating gas, and in the Leblanc process of making soda ash.

155. Refining Sulfur. — The crude sulfur obtained by the above processes is refined by distilling it in earthenware retorts and condensing the vapor in brick chambers; if the temperature of the condensing chamber is below the melting point of sulfur, the vapor is deposited as a fine powder consisting of minute granules and known in commerce as "flowers of sulfur"; if the temperature is above the melting point, the vapor collects on the floor of the room in a liquid state. This is drawn off and cast into large cakes or cylindrical rods, the latter form being known as the roll *brimstone* in commerce.

156. Milk of Sulfur. — A third commercial form, called "lac sulfur," is obtained by precipitation from solution. It is somewhat lighter in color than the other commercial forms and usually contains calcium salts in considerable quantity. It is found in nature as a white deposit at the bottom of sulfur springs.

157. Behavior of Sulfur at Different Temperatures. — At $-50°$ C. sulfur is almost colorless; at ordinary temperature it is a yellow, brittle, crystalline solid; as the temperature is increased a change occurs at 114° C., another between 114° C. and 150° C., a third at 230° C., a fourth between 300° C. and 400° C., and at 448° C. it boils.

Experiment LXIX. — Heat a few grammes of sulfur in a dry test tube. Apply the heat very slowly and describe all changes of color or density which occur. What is the color of the vapor?

158. The Allotropic Forms of Sulfur. — Allotropism is the property certain substances have of existing in two or more conditions which are distinct in their physical or chemical relations.

Experiment LXX. Prismatic Sulfur. Crystallization by Fusion. — Melt a few grammes of sulfur in a test tube, being careful that it does not change color. Pour it into a piece of paper folded as for filtering; as the crystals begin to form, unfold the paper and hold it vertically until the liquid sulfur drains from the crystals. Examine the crystals with a lens. Describe them. Are they soluble in carbon disulfid?

This form is not permanent, but passes slowly into the octohedral form. Its specific gravity is 1.96, a little less than that of the next variety.

Experiment LXXI. Octohedral or Rhombic Sulfur. Crystallization from Solution. — Place half a gramme on a filter paper, pour a little carbon disulfid through the filter into a test bottle; when it is filtered, set the bottle aside for a few hours. Describe the crystals which are found in the bottle after the carbon disulfid has evaporated.

This is the most stable form, and therefore the form which occurs in nature; its specific gravity is 2.05.

Experiment LXXII. Plastic Sulfur. — Heat a few grammes of sulfur in a test tube until it boils, then pour it into a dish of water. Examine it carefully and describe its properties.

Plastic sulfur is not permanent in air, but changes to the octohedral form in a day or so; its specific gravity is 1.96. Is it soluble in carbon disulfid?

A fourth form is a white amorphous substance forming about 5 % of flowers of sulfur, from which it may be separated by dissolving the crystals in carbon disulfid, in which the white amorphous sulfur is insoluble.

Experiment LXXIII. — Examine the forms of sulfur which you have prepared, describe their physical properties, ignite a piece of each, observe the character of the flame and the odor of the gas formed by the combustion of each. What evidence do you obtain that sulfur is allotropic?

There are several other allotropic forms, but they are of minor importance; the differences between them may be attributed to the varying number of atoms in the molecule.

159. Properties. — We have learned some of the more important properties of sulfur from the preceding experiments, but the following additional properties must not be overlooked: —

(*a*) It is insoluble in water.

(*b*) At high temperatures it has a strong affinity for oxygen.

At ordinary temperatures sulfur does not combine with oxygen. When heated to about 260° C. it burns actively and forms sulfur dioxid, SO_2. When one attempts to light it with a match, they will observe that the time required to ignite it depends upon the quantity of sulfur that must be raised to the kindling temperature.

(*c*) Its affinity for metals.

Experiment LXXIV. — Heat a few grammes of sulfur to boiling; hold a spiral of fine copper wire so that the end just dips in the boiling sulfur. What evidence of chemical action do you observe? Is the wire changed in appearance? Is it still pure copper? Test its brittleness and other physical properties.

The great affinity of sulfur for metal is shown by the large number of sulfids found in nature, and also by the activity with which it combines with metals, the union in many cases developing heat and light, as in Experiment 19.

160. Uses. — Sulfur is extensively used in manufacturing certain substances, among which we may mention gunpowder, fireworks, matches, and sulfuric acid; it is also used in the process of vulcanizing caoutchouc, and in the preparation of sulfur dioxid for bleaching and disinfecting.

161. Its Use in Making Lucifer Matches. — The low kindling temperature of sulfur, 260° C., is advantageously applied in making matches. The small amount of phosphorus on the end of the match stick could not raise the wood to its kindling temperature, but it easily raises sulfur to 260° C., and the heat of the burning sulfur ignites the wood. In certain kinds of matches paraffin is used for this purpose instead of sulfur, because of the disagreeable odor of burning sulfur.

The common sulfur match is prepared as follows: The match sticks are dipped in melted sulfur to a depth of about half an inch, and afterward tipped with an emulsion of the following substances: —

Ordinary phosphorus	9 parts
Saltpetre	14 "
Manganese dioxid	14 "
Glue	16 "

SECTION II. — SULFUR DIOXID

FORMULA SO_2. — MOLECULAR WEIGHT 64

162. Occurrence. — This substance exists in the gases evolved by volcanoes, and in solution in the springs of certain volcanic regions. It is one of the constituents of coal gas, and is usually present in the air of cities.

163. Preparation. — Sulfur dioxid is formed when sulfur is burned in air or in oxygen, and for many purposes is best prepared in this way. For experimental purposes the following method is preferred: —

Experiment LXXV. — In a flask place six or eight pieces of sheet copper. Pour 5 or 10 cc. of concentrated H_2SO_4 over it. Arrange the apparatus for collecting gas over water. Heat gently and cau-

tiously. The moment the gas begins to come off, lower the flame, and keep it at such a height that the evolution is regular and not too rapid. After concluding whether or not the gas is soluble in water, collect a bottle by downward displacement. It is more than twice as heavy as air. Determine whether the gas will burn or support combustion. What effect has the solution of the gas on litmus paper? Allow the gas to bubble through a solution of potassium permanganate, a solution of chromic acid, a solution of iodin. What effect has the gas on the color of the solution? Note the physical properties of the gas.

The relation between the factors and the products in this reaction is shown by the following equation: —

$$Cu + 2\ H_2SO_4 = CuSO_4 + 2\ H_2O + SO_2.$$

It is probable, however, that the copper acts upon a molecule of the acid, and that the nascent hydrogen reduces the second molecule of the acid, as was explained in Experiment 57, in which copper apparently reduced nitric acid.

164. Properties. — At ordinary pressure sulfur dioxid is condensed to a liquid at $-10°$ C. If the gas be passed through a tube packed in ice and salt, it is liquefied at ordinary pressure. At ordinary temperatures it liquefies under a pressure of 75 pounds per square inch. The sudden evaporation of liquid sulfur dioxid causes intense cold, and the liquid is often used as a refrigerating agent. Sulfur dioxid is irrespirable and perhaps poisonous. It destroys certain kinds of germs, particularly those which cause fermentation and decay of organic substances. Its effect on disease germs is very much overestimated, but when used in large quantity it is a valuable disinfectant. Sulfur dioxid combines with water to form sulfurous acid, H_2SO_3, which has a strong affinity for oxygen, and which takes it from many substances. In certain cases sulfur dioxid is said to bleach moist substances by abstracting the oxygen

from the water, the nascent hydrogen *reducing* the coloring matter, a process which is the reverse of that by which chlorin destroys color. In other cases the bleaching action is due to the formation of a colorless compound by the sulfur dioxid and the pigment, and in such cases the color may be restored by any chemical which will decompose the compound formed. The yellow color which flannel gradually acquires when washed with soap is an illustration of the power of alkalies to restore the original color of substances bleached with sulfur dioxid.

165. Uses. — It is extensively used in bleaching straw, silk, and woollen goods, or any material that would be injured by chlorin. There are two processes: —

First. — By suspending the article to be bleached in the fumes of burning sulfur.

Second. — By immersing the substance in an aqueous solution of the gas.

Experiment LXXVI. — Suspend a colored flower in a bell jar and burn sulfur under it. After the flower is bleached, dip it into dilute sulfuric acid. What occurs?

As sulfur dioxid prevents fermentation, it is sometimes used in preserving fruit juice. The juices are treated with some substance that gives off the gas slowly, *e.g.* any sulfite.

Note. — The writer is unable to see why a substance which will prevent fermentation in the air should not prevent fermentation in the stomach, or digestion, thus rendering the articles of food preserved in this way worse than useless.

Sulfur dioxid is sometimes used to extinguish fires in closed rooms or chimneys. If sulfur is thrown on the fire, it is ignited, using up the oxygen and filling the space with a non-supporter of combustion.

Liquid sulfur dioxid produces intense cold if rapidly evaporated, and is sometimes used for freezing purposes; it is also extensively used as a disinfectant, in the manufacture of sulfuric acid, and as an antichlor in paper mills.

SECTION III. — HYDROGEN SULFID

FORMULA H_2S. — MOLECULAR WEIGHT 34

166. Occurrence. — This compound issues from the earth in volcanic regions; decomposing organic substances containing sulfur evolve it, and the water of sulfur springs owes its characteristic properties to the dissolved hydrogen sulfid present.

167. Preparation. — (*a*) Hydrogen sulfid may be formed by synthesis, by passing streams of hydrogen and sulfur vapor through a hot porcelain tube. (*b*) In the laboratory it is usually prepared by decomposing a sulfid with an acid.

Experiment LXXVII. — 1. Arrange your apparatus as for preparation of hydrogen, page 42.

2. Place a few grains of iron sulfid in the generating bottle and cover it with dilute sulfuric acid. Collect two bottles of the gas over water; test the water with litmus paper.

3. Is the gas soluble in water?

4. Determine whether the gas should be collected by upward or downward displacement, and fill three bottles.

5. Is the gas combustible or a supporter of combustion?

6. Devise a test which will show whether the gas is explosive when mixed with air.

7. Apply a lighted match to the mouth of a bottle of the gas, and look for evidence of the formation of water, or sulfur dioxid, or both. Which element of the hydrogen sulfid is deposited on the sides of the bottle?

8. Pass H_2S successively through solutions containing lead nitrate, zinc sulfate, copper sulfate, cadmium chlorid, and arsenic chlorid. What do you observe in each case? The substances formed are re-

spectively the sulfids of lead, zinc, copper, cadmium, and arsenic. The reaction in the case of copper sulfate is as follows: —

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

9. Describe the odor of the gas and the character of its flame. When hydrogen sulfid is prepared by treating iron sulfid with sulfuric acid the following reaction occurs: —

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

168. Properties. — Hydrogen sulfid is a powerful poison. In an abundant quantity of air it burns, forming sulfur dioxid and water. When the supply of oxygen is limited one of the elements is not completely consumed, as was shown in Experiment 77. At ordinary pressures, hydrogen sulfid is liquefied at $-62°$ C.; at ordinary temperatures it also liquefies when subjected to a pressure of about seventeen atmospheres. The acid reaction of the aqueous solution of hydrogen sulfid has led chemists to consider it an acid, and it is often called hydrosulfuric acid; the sulfids are considered its salts. Hydrogen sulfid is very unstable; at a temperature slightly above 400° C. its molecule is broken up; it is decomposed by all of the halogens; many metals act upon it at ordinary temperatures, replacing its hydrogen and forming sulfids. Because of its instability, hydrogen sulfid often acts as an excellent reducing agent, its efficiency being due to the action of nascent hydrogen.

169. Uses. — Hydrogen sulfid is extensively used in chemical analysis. When a solution containing certain basic elements is treated with this gas, a sulfid is formed which may be recognized by its color, or by its behavior when treated with certain solvents. Several sulfids are insoluble in an acid solution, and are, therefore, deposited as solids, or precipitated, when gas is passed into an acid solution containing them. Others are soluble in an acid, but

insoluble in an alkaline solution, and are therefore precipitated from alkaline solutions. Still others are soluble in water, and remain in solution. These properties form the basis of the system of qualitative analysis generally used.

170. Test. — (*a*) *For Hydrogen Sulfid.*

1. The free gas may be detected by its odor.

2. A piece of filter paper moistened with lead acetate is blackened by the gas.

(*b*) *For Sulfids.*

1. Sulfids are decomposed by hydrochloric acid, with evolution of hydrogen sulfid, which may be recognized as in (*a*).

2. Pulverize the substance to be tested, mix with sodium carbonate, Na_2CO_3, on a bit of porcelain or platinum foil, and fuse it in the Bunsen flame. Place the fused mass on a clean silver coin and add a drop of water. If a sulfid be present, a black spot will appear on the silver. Silver is blackened by vulcanized rubber and by eggs. What does this indicate?

SECTION IV. — SULFURIC ACID

(OIL OF VITRIOL)

FORMULA H_2SO_4. — MOLECULAR WEIGHT 98

171. Occurrence. — Small quantities of sulfuric acid are found in some rivers and springs in volcanic regions; its salts are quite abundant.

172. Preparation. — Sulfuric acid cannot be easily prepared from its salts, but is manufactured on a large scale by oxidizing sulfurous acid; the chemical changes involved in the process are rudely illustrated in the following experiment.

Experiment LXXVIII. — Pour water into your largest bottle to a depth of about one inch, lower burning sulfur into the bottle, using an ignition spoon ; cover the bottle with a glass plate. After the sulfur is extinguished, stir the sulfur dioxid in the bottle with a glass rod dipped in nitric acid. Is there any evidence of the formation of nitrogen peroxid ? Of nitric oxid ? When the sulfur dioxid has changed color, cover the bottle with the hand and shake it, dissolving the gases. Repeat the process three times over the same layer of water ; bring a sample of the sulfuric acid thus formed to the desk to be tested.

173. The Chemical Changes involved in this process are indicated in the following reactions : —

$$SO_2 + H_2O = H_2SO_3,$$

$$H_2SO_3 + O = H_2SO_4.$$

Nitric acid is used to hasten this oxidation of the sulfurous acid, which takes place very slowly in air; its action is represented thus : —

$$2\,HNO_3 + 3\,SO_2 + 2\,H_2O = 3\,H_2SO_4 + 2\,NO.$$

Nitric acid is much more expensive than sulfuric, and if it were not for the interesting action of the nitric oxid formed in the last reaction, nitric acid could not be used for this purpose. It will be remembered that nitric oxid takes oxygen from the air, forming nitrogen peroxid, and that nitrogen peroxid is an excellent oxidizing agent. The nitrogen peroxid converts another molecule of sulfurous acid into sulfuric acid, and is again reduced to nitric oxid thus : —

$$NO + O = NO_2,$$

$$NO_2 + H_2SO_3 = H_2SO_4 + NO.$$

The nitric oxid therefore acts as a carrier of oxygen from the air to the sulfurous acid, alternately abstracting it from the air and giving it up to the sulfurous acid ; theoretically

there is no limit to the number of molecules of sulfurous acid that may be oxidized by a single molecule of nitric oxid.

174. Manufacture of Sulfuric Acid. — On a manufacturing scale this reaction is carried on in lead-lined chambers usually about 100 feet long, 20 feet wide, and 20 feet high, several of these chambers being connected so that the gases may pass from one to another. Lead is selected for this purpose because dilute sulfuric acid does not dissolve it. No other metals can be used with the lead, as electric action would ensue, and one of the metals would be dissolved. The leaden chamber must therefore be lined without solder and without nails; the sheets of lead are joined by melting the edges with an oxyhydrogen blowpipe and are supported by straps of lead fastened to the outside of the lining.

At one end of a series of such chambers are furnaces in which sulfur dioxid is formed by burning sulfur or iron pyrites in a supply of air which is carefully controlled to prevent too great dilution of the gases or too small a supply of oxygen. The gas from these furnaces heats the "nitre pots," or vessels containing potassium nitrate and sulfuric acid, which form nitric acid. From this point, the air, sulfur dioxid, and nitric acid are conducted to the leaden chambers. Jets of steam pour into the chambers at frequent intervals. At the end of the last chamber of the series is a leaden tower filled with coke; a spray of strong sulfuric acid flows in at the top of this tower and absorbs nitrogen peroxid and returns it to the chamber. From this tower the gases pass into a tall chimney which creates a strong draft and causes the circulation of the gases within the chamber.

The acid formed is collected on the floor of the chamber, and is removed when rather dilute, as the strong acid dis-

solves the lead. It is then heated in glass or platinum stills until it contains only two per cent of water, when it is ready for the consumer.

175. Properties. — (*a*) At ordinary temperature pure sulfuric acid is a colorless, oily liquid 1.8 times heavier than water. At 10.5° C. it freezes. (*b*) It has a marked affinity for water; when mixed with it much heat is evolved, and a contraction in volume takes place. Sulfuric acid does not evaporate at ordinary temperatures, but absorbs moisture from the air, increasing in volume quite rapidly in moist weather unless kept in tightly stoppered bottles. Many organic substances containing hydrogen and oxygen are decomposed by sulfuric acid, these elements being extracted in the proportions in which they form water. Experiment 2 illustrates this fact. Wood is charred by the acid, because it loses its hydrogen and oxygen. (*c*) Sulfuric acid forms several definite compounds with water, the greatest amount of heat being developed when two molecules of water combine with one of sulfuric acid. (*d*) At high temperatures sulfuric acid forms more stable compounds with the bases than most other acids, and therefore when sulfuric acid is heated with a salt, a sulfate is formed and the acid which the salt contained is liberated. Nearly all processes of preparing acids are based upon this ability of sulfuric acid to decompose salts.

176. Uses. — Sulfuric acid is our most important reagent. Most chemical industries depend upon it; *e.g.* the refining of petroleum, also the manufacture of artificial fertilizers, phosphorus, sodium carbonate, and alum. In the laboratory it is used for drying gases, in the preparation of most acids, and in many other reactions with several of which the student is already familiar.

REVIEW QUESTIONS

1. In what four allotropic forms does sulfur occur? What does allotropic mean?

2. In what forms is sulfur known in commerce?

3. State the color, odor, weight, and state of sulfur dioxid.

4. Describe the extraction of sulfur from its ores, and discuss its behavior at different temperatures.

5. Compare the crystals of sulfur formed by solution with the crystals of sulfur formed by fusion.

6. Describe the manufacture of matches.

7. Describe the preparation of hydrogen sulfid. Give equation.

8. For what is hydrogen sulfid used in the chemical laboratory? Discuss its instability.

9. What inorganic substance is found in vulcanized rubber? How may the rubber be tested for its presence?

10. Describe the manufacture of sulfuric acid; write the reactions which take place, and give its uses.

11. For what purpose is nitric acid used in the manufacture of sulfuric acid?

12. Describe the method of preparing sulfur dioxid from sulfuric acid. State two purposes for which sulfur dioxid is used in large quantities.

CHAPTER XVI

CERTAIN CHEMICAL RELATIONS

177. Basicity of Acids. — An acid which contains only one replaceable hydrogen atom is said to be *monobasic*. Hydrochloric and nitric acids belong to this class.

An acid which contains two replaceable hydrogen atoms is said to be *dibasic*. Sulfuric acid, H_2SO_4, and carbonic acid, H_2CO_3, belong to this class. The terms *tribasic*, *tetrabasic*, etc., are applied to acids having three, four, etc., replaceable hydrogen atoms.

A dibasic acid may form a compound with certain basic elements like sodium, in which only one of the hydrogen atoms is replaced; the salt thus formed frequently reddens blue litmus paper and has the power to neutralize more of the basic element; as it retains some of the properties of the acid, it is called an *acid salt*. The salt formed when both of the hydrogen atoms are replaced is an entirely distinct substance and is called a *normal salt*. Hydrochloric and nitric acids can form but one salt with a given element, but the dibasic acids may form two salts with a single metal as is illustrated below: —

ACID SALTS

Potassium acid sulfate,	$HKSO_4$
Sodium acid sulfate,	$HNaSO_4$
Potassium acid carbonate (saleratus),	$HKCO_3$
Sodium acid carbonate (baking soda),	$HNaCO_3$

NORMAL SALTS

Potassium sulfate,	K_2SO_4
Sodium sulfate,	Na_2SO_4
Sodium carbonate (washing soda),	Na_2CO_3
Potassium carbonate (pearl-ash),	K_2CO_3

Acids of higher basicity also form both acid and normal salts.

An acid salt is one that contains replaceable hydrogen.

A normal salt is one in which the whole of the replaceable hydrogen has been replaced by the base.

178. The Theory of Valence. — Considering the formulas of the binary compounds of hydrogen, we observe that the elements differ in respect to the number of atoms of hydrogen with which they combine, and that they may be arranged in classes upon this basis. The following formulas illustrate this fact: —

I	II	III	IV
HF	H_2O	NH_3	CH_4
HCl	H_2S	PH_3	SiH_4
HBr	H_2Se	AsH_3	
HI			

The formulas of the chlorids show a similar difference in the number of atoms of the hydrogen of hydrochloric acid which the elements can replace, thus: —

I	II	III	IV	V
NaCl	$CaCl_2$	$BiCl_3$	$SnCl_4$	PCl_5
KCl	$BaCl_2$	$SbCl_3$	CCl_4	
AgCl	$ZnCl_2$			

The ability of an element to combine with or replace hydrogen is called valence.

Elements are said to be *univalent, bivalent, trivalent,* etc., as they combine with or replace one, two, three, etc., atoms of hydrogen.

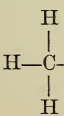
The terms monad, dyad, and triad are sometimes used instead of univalent, bivalent, and trivalent, but the latter terms are to be preferred.

VALENCE OF THE ELEMENTS

Univalent		Bivalent		Trivalent		Quadrivalent	
F	19	O	16	Sb	120	Al	27
Cl	35.5	S	32	As	75	C	12
Br	80	Ca	40	Bi	208	Cr	52
I	127	Sr	87.5	B	11		
H	1	Ba	137	P	31		
Na	23	Cd	112	N	14		
K	39	Fe	56				
Li	7		63				
Ag	108	Sn	118				
Au	186	Zn	65				
		Hg	200				

The valence of an element is often indicated by Roman numerals written above the symbol to the right, thus: —

Fe^{IV} indicates quadrivalent iron. Valence may also be indicated in graphic formula by the number of lines drawn to a symbol, thus, CH_4 may be written: —



H—O—H.

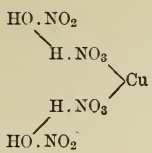
Although the valence of many of the elements appears

to be variable, the classification is of great assistance in writing the formulas of the common compounds. Thus, if one desires to write the formula of the sulfate of a univalent element, he knows that there must be as many atoms of the element as there are atoms of hydrogen in sulfuric acid; *i.e.* he considers that the sulfate is formed by replacing the hydrogen of the acid with the given element. Potassium sulphate, K_2SO_4, may be taken as a type of the sulfates of univalent metals; calcium sulfate, $CaSO_4$, as a type of the sulfates of bivalent metals; and antimony sulfate, $Sb_2(SO_4)_3$, of trivalent metals.

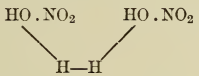
179. The Nascent State.

The term *nascent state* is convenient, but is not very accurate, because it implies that the substance to which it is applied has been liberated from some compound, and exists in some unusual form or state in which it possesses unusual chemical energy, whereas the nascent element does not exist in the free state at all, but passes directly from the molecule of the factor to that of the product. The lesser chemical energy in its normal state is, no doubt, due to the fact that two or more atoms of the element are united to form a molecule, and, whatever the nature of the force which holds them together, energy must be expended to overcome it before the atoms can form new combinations. Now, in the case of the so-called nascent element it will be seen that the chemical change involves at least three molecules, that one of these molecules has the power to decompose a second molecule and replace some of its atoms, and that the third molecule is, therefore, acted upon by the full chemical energy of the nascent atom.

The following diagrams will assist the student to understand the increased chemical activity of nascent hydrogen. An atom of copper has the power to displace the hydrogen of two molecules of the acid forming copper nitrate, $Cu(NO_3)_2$. The copper atom attracts the NO_3 group of atoms, and then hydrogen is at the same time attracted by the HO group of a neighboring molecule of nitric acid, and, under the action of these forces, a rearrangement of the atoms is effected, forming, at the same instant, molecules of copper nitrate, water, and nitrogen peroxid.



If hydrogen gas be passed through nitric acid, the case is quite different. The hydrogen atoms are held together by a certain force, and the HO group is held to the NO_2 group. The attraction between the atom of hydrogen and the HO group is not great enough to overcome the attraction between the hydrogen atoms and to separate the HO and the NO_2 groups at the same time.



In the nascent state, then, monatomic elements should not show increased activity, while all others should.

180. Avogadro's Law. — An Italian physicist named Avogadro, who had been studying the specific gravities of aeriform bodies, in 1811 announced his belief that *under like conditions of temperature and pressure equal volumes of all gases, whether simple or compound, contain the same number of molecules.* Although this important law was not at once accepted, it can now be shown mathematically that in order that equal volumes of gases may expand and contract equally under like changes of temperature or pressure, it is necessary that each volume contain the same number of molecules.

181. Some Deductions from Avogadro's Law. — 1. It will be observed that the vapor densities and the atomic weights of the first nine elements in the following table are numerically equal. There are, therefore, in equal volumes of these elements the same number of atoms, and as there are also

the same number of molecules in the equal volumes, it follows that *there must be the same number of atoms in each molecule of each of the nine elements.*

TABLE OF VAPOR DENSITIES AND ATOMIC WEIGHTS

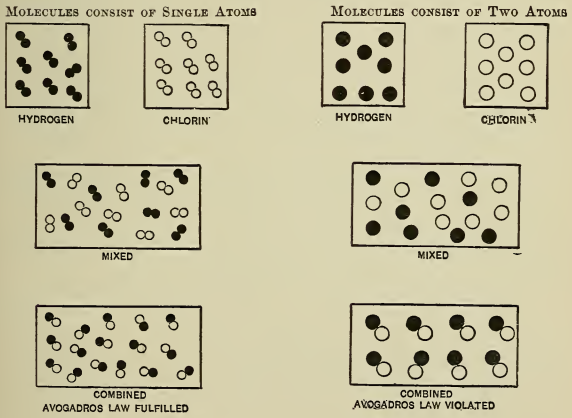
ELEMENTS	Atomic Weight	Molecular Weight	Vapor Density
Hydrogen	1	2	1
Nitrogen	14	28	14
Oxygen	16	32	16
Fluorin	19	38	19
Sulfur	32	64	32
Chlorin	35.5	71	35.5
Selenium	79	158	79
Bromin	80	180	80
Iodin	127	254	127
Sodium	23	23	11.5
Potassium	39	39	19.5
Zinc	65	65	32.5
Cadmium	112	112	56
Mercury	200	200	100
Phosphorus	31	124	62
Arsenic	75	300	150

COMPOUNDS	Molecular Weight	Vapor Density
Water, H_2O	18	9
Hydrochloric acid, HCl	36.5	18.25
Hydrobromic acid, HBr	81	40.5
Hydriodic acid, HI	128	64
Ammonia, NH_3	17	8.5
Carbon monoxid, CO	28	14
Carbon dioxid, CO_2	44	22
Nitrogen monoxid, N_2O	44	22

2. It has been proven experimentally that one litre of hydrogen and one litre of chlorin form two litres of hydrochloric acid; hence, according to Avogadro's law, x molecules of hydrogen plus x molecules of chlorin form $2x$ molecules of hydrochloric acid; but in $2x$ molecules of hydrochloric acid there are $2x$ atoms of hydrogen, therefore in each molecule of hydrogen there must be at least two atoms of hydrogen; and further, *the molecules of each of the first nine elements in the table must contain at least two atoms.*

Molecules which consist of two atoms are said to be diatomic.

The following diagrams will assist the student in following this line of thought:—



In the above diagrams an atom of hydrogen is represented by the symbol ●, and one of chlorin by ○. The size of the squares accords with the fact that one volume of hydrogen and one volume of chlorin form two volumes of hydrochloric acid.

3. The *atomic* weights of sodium, potassium, zinc, and cadmium, are respectively twice their vapor densities. That is to say, whereas the atom of sodium is 23 times as heavy as the atom of hydrogen, a litre of sodium vapor is only 11.5 times as heavy as a litre of hydrogen. Hence, in a litre of sodium vapor there are only half as many atoms as there are in a litre of hydrogen. But according to Avogadro's law, the number of molecules in the litre of sodium vapor is the same as the number of molecules in the litre of hydrogen; therefore, *there are only half as many atoms in a molecule of sodium as there are in a molecule of hydrogen.* If the hydrogen molecule is diatomic, the sodium molecule is monatomic, and so also are the molecules of potassium, zinc, and cadmium. Similar reasoning shows that *the molecules of phosphorus and arsenic have twice as many atoms as the molecule of hydrogen.* If hydrogen is diatomic, these elements are tetra-atomic, and the molecular weight is four times their atomic weight.

4. *It will be observed that the density of any gas or vapor is numerically equal to half its molecular weight.* This is due to the fact that molecular weights are expressed in terms of the weight of an atom of hydrogen, while the density is based upon the weight of a molecule of hydrogen.

5. Inasmuch as there are equal numbers of molecules in equal volumes of all gaseous substances, we may learn from an equation expressing chemical action between gases the relative volumes of each of the factors and products, provided we are careful to write the reactions so that they express the relation between molecules instead of atoms. The equation

$$H + Cl = HCl$$

is an *atomic* equation because two of the terms represent atoms, but if we write it thus,

$$H_2 + Cl_2 = 2\ HCl,$$

it represents the action as taking place between molecules. From this equation we see that one molecule of hydrogen unites with one molecule of chlorin to form two molecules of hydrochloric acid; therefore, one volume of hydrogen unites with one volume of chlorin to form two volumes of hydrochloric acid.

The equation $N_2 + 3\ H_2 = 2\ NH_3$

shows us that one volume of nitrogen unites with three volumes of hydrogen to form two volumes of ammonia. *Every molecular equation which represents a reaction between gases expresses the volumetric relations of the factors and products.*

REVIEW QUESTIONS

1. Give the symbols of a dibasic acid and the symbols of their salts which fully illustrate the basic properties of that acid.
2. Name, define, and illustrate two great classes of salts.
3. Write names and symbols of three univalent elements, three bivalent elements, and three trivalent elements.
4. State the theory of valence.
5. When are elements said to be in a nascent state? What peculiarity do most substances exhibit when in this state? Illustrate.
6. What does the following equation teach us concerning the volumetric composition of water: —

$$2\ H_2 + O_2 = 2\ H_2O.$$

7. State the composition of sulfur dioxid by weight and by volume.
8. State the valence of the metals forming chlorids having the following formulas: $CaCl_2$, KCl, NaCl.
9. Sulfur forms a compound having the formula SH_2. What is the valence of the sulfur?

CHAPTER XVII

THE ALKALI METALS

SECTION I. — POTASSIUM AND ITS COMPOUNDS

182. Thus far we have considered only acid-forming elements. It is true that some of them manifest basic properties when combined with the stronger acid-forming elements, but considering all of their properties, they are classed with the acid-formers. We can have only time to discuss the most important basic elements, and a few of their compounds. The principal alkali metals are lithium, potassium, and sodium. Ammonium is treated as a member of this family because of its strong basic properties, but it must be remembered that it is a radical and not an element.

POTASSIUM

SYMBOL K. — ATOMIC WEIGHT 39

183. Occurrence. — Potassium is not found free in nature; in combination, chiefly as a silicate it occurs in many minerals. The older rocks, such as granite and gneiss, contain a large percentage of feldspar, a silicate of aluminum and potassium. Potassium compounds are necessary constituents of all fruitful soils. They are absorbed by the plants, none of which can live without them.

184. Preparation and Properties. — At one time the chief source of this element was wood ashes, from which it may be obtained as a carbonate. Now the chief source is the

deposit of potassium salts found near Stassfurt in Germany. Metallic potassium is prepared by distilling the carbonate with charcoal, with the following reaction: —

$$K_2CO_3 + 2\,C = 2\,K + 3\,CO.$$

Potassium is a light metal with a bright metallic lustre, it floats on water, decomposing it with the evolution of sufficient heat to ignite the hydrogen liberated. The following equation explains the reaction which occurs: —

$$K + H_2O = KOH + H.$$

It oxidizes rapidly and must be kept under naphtha or some liquid which does not contain oxygen. Potassium and its compounds communicate a violet tint to flame.

Experiment LXXIX. — Drop a small piece of potassium in water. Describe fully all that occurs. Note the color of the flame. What gas has evolved? What remained in solution? Is it an acid or a base? Test the water with litmus.

185. Potassium Hydroxid, KOH (Caustic Potash). — This substance is prepared by heating potassium carbonate with slacked lime in an iron vessel. In what other way may it be prepared? It is a white, brittle solid, usually cast into sticks, is extremely deliquescent,[1] and dissolves in water with evolution of heat. It is one of the strongest bases known, and is therefore an important reagent in the laboratory. It is also used in the manufacture of Bohemian glass and of soft soap. It attacks the flesh, and is sometimes used as a cautery.

186. Potassium Nitrate, KNO_3 (Saltpetre). — The occurrence of this salt is discussed on pages 40 and 76. It is formed in warm climates by the action of microbes on

[1] Define term.

organic refuse rich in nitrogen. Saltpetre plantations, where the salt is prepared artificially from soil in the neighborhood of ancient villages which has became saturated with animal refuse, are found in India, but the greater part of the potassium nitrate is now obtained by treating sodium nitrate with potassium chlorid. Potassium nitrate is a colorless crystal, very permanent in air, and easily soluble in water. It is an excellent oxidizing agent. Because of its permanence in air, it is extensively used in the manufacture of gunpowder and in pyrotechny.

187. Gunpowder is a mixture of saltpetre, charcoal, and sulfur, the proportion varying somewhat in the different grades, but it is approximately as follows: —

Saltpetre	75 %
Charcoal	15 %
Sulfur	10 %

Its explosive power is due to a complex chemical change which converts about half of its weight into gases; the remainder of the powder forms solids which cause the "smoke," and which render frequent cleaning of the gun necessary. The explosion of ordinary gunpowder forms seven different gases and ten solids. The smokeless powders are converted into gases only.

188. Potassium Chlorate, $KClO_3$, is chiefly valuable as an oxidizing agent. It is used in making parlor matches, in fireworks, medicine, and dyeing.

Experiment LXXX. — Place a little potassium chlorate in a beaker, cover it with water, drop a small piece of phosphorus into the water, and pour about ½ cc. of concentrated sulfuric acid through a funnel tube which extends to the bottom of the beaker. Does combustion

take place? What substances present might furnish oxygen for combustion? Did it occur before the sulfuric acid was added? Does it occur if potassium chlorate is absent? Try it. Whence does the oxygen come? State the physical properties of potassium chlorate.

189. Potassium Carbonate, K_2CO_3. — In America this salt is usually prepared by leaching wood ashes. The ashes are placed in a barrel, water is poured on them and drawn off at the bottom. It dissolves the soluble salts. The potash lye thus obtained contains considerable quantities of potassium carbonate. The salt is prepared from the liquid by evaporation, and is known as potash. When refined it is called *pearl-ash*. It is a deliquescent salt with a strong alkaline reaction.

190. Potassium Acid Carbonate, $KHCO_3$ (Saleratus). — This familiar salt is prepared by passing a current of carbon dioxid through a solution of the normal carbonate.

Uses. — Cooking, bleaching hair.

SECTION II. — SODIUM

Symbol Na. — Atomic Weight 23

191. Occurrence. — The compounds of sodium are widely distributed, and some of them are found in enormous deposits. The chlorid is the most abundant, but large deposits of the nitrate, carbonate, silicate, and borate are found in certain parts of the world.

192. Preparation and Properties. — Sodium is prepared by distilling sodium carbonate with charcoal. It resembles potassium in its physical and chemical properties. It floats on water, decomposing it, but does not always ignite the evolved hydrogen. It oxidizes rapidly in the presence of moisture, and is used as a reducing agent in the prep-

aration of certain metals. When sodium and potassium are melted together under petroleum, an alloy is formed which is a liquid at ordinary temperatures, and which is used in themometers for measuring high temperatures which would vaporize mercury. Sodium and all of its compounds impart a yellow color to flame.

193. Sodium Hydroxid, NaOH (Caustic Soda), like potassium hydroxid, is prepared by boiling a solution of sodium carbonate with calcium hydroxid. It resembles potassium hydroxid in appearance and in chemical properties, but does not deliquesce as rapidly. It is used in the manufacture of glass and soap and in many chemical processes.

194. Sodium Chlorid, NaCl, was formerly obtained by evaporating sea-water, but the discovery of large natural deposits of "rock salt" has diminished its value so as to render this process unprofitable in most countries. At Piffard and at Warsaw, N.Y., salt is taken from the mine in solid form. If the salt is mixed with earthy impurities, water is allowed to flow into the mines, and after a time is pumped out and evaporated. Sodium chlorid crystallizes in transparent cubes; it is necessary to animal life. In the arts, it is extensively used in the alkali industry, in the process of glazing earthenware, in reducing silver, and in preserving meats and fish.

195. Sodium Carbonate, Na_2CO_3. — This salt is the alkali of the arts, and is almost as extensively used as sulfuric acid; in the manufacture of glass and soap large quantities are annually consumed. It occurs in nature in some of the western states, and also in Hungary and in Africa. Prior to 1808 sodium carbonate was obtained from the ashes of sea-plants, which extract it from the salt water just as land

plants absorb potassium from the soil; but during the French Revolution, the government being unable to obtain it, offered a large reward for a process of making it from common salt. Leblanc won the prize, and the process which bears his name has been extensively used ever since. In the *Leblanc process* sodium chlorid is first heated with sulfuric acid in a covered cast iron pan, *D* (figure 16). The hydrochloric acid formed is conducted to the condensing

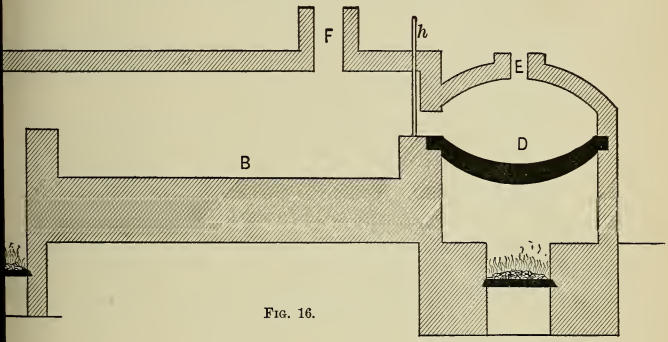


Fig. 16.

towers through the pipe *E*; when the mass begins to solidify, the slide *h* is raised and the mass raked out onto the hearth *B* of a reverberatory furnace. Here it is heated to dull redness by a coke fire at *A*. This converts the salt into the normal sodium sulfate,—

$$2\,NaCl + H_2SO_4 = 2\,HCl + Na_2SO_4.$$

The acid evolved during this process is also conducted to the condensing towers through the pipe *F*. The "salt cake" taken from the hearth is mixed with limestone (calcium carbonate) and coal dust, and again heated to a high tem-

perature on the hearth of a furnace, when the following reaction occurs: —

$$Na_2SO_4 + CaCO_3 + 2\,C = Na_2CO_3 + CaS + 2\,CO_2.$$

The *black ash* formed in this furnace contains something less than half its weight of sodium carbonate. The other substances found in the black ash are insoluble in water; the sodium carbonate is therefore dissolved out. The solution is evaporated and the residue calcined at a red heat. This forms a nearly pure, anhydrous sodium carbonate known in commerce as *soda-ash*. If it is redissolved and allowed to crystallize, the common *washing soda* is obtained, having the composition Na_2CO_3, $10\,H_2O$.

In the *Solvay process*, which is much cheaper than the Leblanc, ammonia is passed through tanks containing brine. This precipitates magnesia and calcium carbonate, and raises the temperature of the liquid, which is decanted, filtered, and cooled, and then passed through the carbonating tower. The tower is about 50 feet high and 6 feet in diameter. At intervals of about 3 feet there are compound diaphragms consisting of a horizontal plate with a large hole in the centre, and over this a curved plate perforated with small holes and deeply notched around the edge. The brine is introduced near the top, and carbon dioxid is forced into the brine near the bottom of the tower and passes upward through the holes in the diaphragms. In this tower the principal reaction occurs: —

$$NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl.$$

The hydrogen sodium carbonate thus formed is less soluble than the ammonium chlorid; it therefore crystallizes first as the solution approaches saturation, and collects at the bottom of the tower. The ammonium chlorid formed

is treated with calcium hydrate, and the ammonia liberated is used to saturate more of the brine. A lime-kiln is usually maintained in connection with Solvay plants, to furnish the lime used in recovering the ammonia, and most of the carbon dioxid required is obtained from the waste gases of the kiln. It thus appears that the raw materials required for the Solvay process are common salt, limestone, and a supply of ammonia which is used over and over again. The materials required for the Leblanc process are common salt, sulfuric acid, limestone, and coal, neither of which is used again.

Notwithstanding the fact that hydrogen sodium carbonate is the only product as yet obtained from the Solvay process, whereas the Leblanc process yields hydrochloric acid and sulfur in addition to sodium carbonate, the greater cost of the raw material, together with the inferior quality of the Leblanc product, places the Leblanc process at such a disadvantage that at the present time the Solvay process supplies considerably more than half of the soda-ash of commerce. The hydrogen sodium carbonate is converted into normal carbonate by calcination.

196. Hydrogen Sodium Carbonate, $HNaCO_3$ (Sodium Bicarbonate or Baking Soda). — This substance may be prepared by passing carbon dioxid through large cylindrical towers filled with the normal carbonate, but the greater part of the hydrogen sodium carbonate of commerce is prepared by the Solvay process, described in the preceding article. Its crystals contain no water of crystallization; they dissolve readily in eleven parts of water, the solution having a feeble alkaline reaction. Boiling a solution of this salt disengages carbon dioxid, converting the salt into the normal carbonate. It is a valuable reagent in the laboratory,

is the principal alkali used by cooks, and is used in medicine to a limited extent.

197. Baking Powders are mixtures which evolve gas when moistened, and are chiefly used as substitutes for yeast. A common form is prepared by mixing cream of tartar, $KH_5C_4O_6$, 56 %; hydrogen sodium carbonate, 25 %; and starch, 19 %. Tartaric acid is sometimes used instead of cream of tartar, but these powders do not keep as well as the above. When this mixture is moistened, carbon dioxid is evolved as it is during fermentation, and the purgative Rochelle salts remain in solution. When cake or biscuits are raised with baking powder the escaping carbon dioxid renders the dough light. Professor Horsford has patented a baking powder consisting of dried phosphoric acid and hydrogen sodium carbonate. Carbon dioxid is evolved, and sodium phosphate remains in the dough. The best baking powder of the ordinary class is one containing only cream of tartar and hydrogen sodium carbonate, but these powders do not retain their leavening power very long unless starch or some equivalent is added. Many of the commercial articles contain either alum or ammonium carbonate, and some of them contain both.

SECTION III. — AMMONIUM SALTS

198. The compounds of the radical NH_4 are treated here because they resemble those of sodium and potassium. In its chemical affinities ammonium behaves like a basic element.

199. Ammonium Chlorid, NH_4Cl, is prepared by neutralizing the ammoniacal liquor of the gas works with hydrochloric acid and evaporating the solution to dryness, the residue is heated in iron vessels, when ammonium chlorid sublimes.

It has a sharp, saline taste, is soluble in water, and, when heated in contact with a metal, it either dissolves the coating of oxid (rust) on the metal or converts it (the rust) into a chlorid, thus leaving a bright surface.

Because of this property it is extensively used in soldering and in galvanizing and tinning metals. When heated it sublimes, that is to say, it passes from a solid state into a vapor without perceptible liquefaction. Ammonium chlorid is commonly called sal ammoniac. It is largely used as the exciting liquid in batteries and is also employed in calico printing and in medicine.

200. Ammonium Nitrate is prepared by neutralizing nitric acid with ammonia and evaporating the solution until it crystallizes on cooling.

When heated rapidly, as by contact with a red-hot metal, it detonates, as it does also when heated in contact with organic matter. It dissolves readily in water, producing a marked drop in temperature.

Uses. — Preparing nitrogen monoxid, in certain explosives, also in freezing mixtures.

201. Ammonium Carbonate. — The commercial article (sal volatile or "smelling salts") is a somewhat unstable mixture of hydrogen ammonium carbonate and ammonium carbonate which smells strongly of ammonia. The normal carbonate, $(NH_4)_2CO_3$, and the acid carbonate, $(NH_4)HCO_3$, are easily obtained.

Uses. — In medicine, in the laboratory, and by bakers. It is the cause of the odor of ammonia frequently detected in bakers' cake.

202. Ammonium Sulfid, $(NH_4)_2S$. — The principal use of this substance depends upon the ease with which it is de-

composed by the compounds of certain bases. These bases are precipitated as sulfids, and thus may be easily separated from other elements in the process of qualitative analysis. The solution of ammonium sulfid forms a colorless liquid of disagreeable odor, which gradually turns yellow because of the formation of compounds known as poly-sulfids of ammonia, having the formulas $(NH_4)_2S_2$; $(NH_4)_2S_3$; etc.

203. Ammonium Hydrosulfid, NH_4HS. — This substance corresponds to the acid salts in having only one of the hydrogen atoms of hydrogen sulfid replaced.

The compounds of the alkali metals, including ammonium, are isomorphous. Their chemical properties are related to their atomic weights.

REVIEW QUESTIONS

1. What is baking powder? What is the theory of its action?
2. What is gunpowder? Describe its manufacture.
3. State a method of preparation of an aqueous solution of potassium hydroxid from metallic potassium.
4. Give the names, formulas, and uses of three important compounds of sodium. Describe some process of making sodium carbonate.
5. State the composition of black gunpowder and explain the function of each of the chemicals.
6. Discuss the physical and chemical properties of potassium.
7. How is ammonium nitrate prepared? What substances are formed when it is decomposed by heat?
8. Define isomorphous. (Consult dictionary.)
9. For what purpose have you used ammonium nitrate? What occurs when it is heated?

CHAPTER XVIII

CALCIUM

Symbol Ca. — Atomic Weight 40

204. Occurrence. — In combination with other elements, calcium occurs in enormous quantities. Limestone, marble, and chalk are calcium carbonate, $CaCO_3$. Gypsum is calcium sulfate, $CaSO_4$; fluorspar is calcium fluorid, CaF_2. A natural phosphate, $Ca_3(PO_4)_2$, occurs in large quantities in Florida.

205. Preparation and Properties. — Calcium is prepared by electrolizing fused calcium chlorid. It is a yellowish metal, many times more valuable than gold. Like potassium and sodium, it decomposes water and cannot be kept in moist air; it is seen only in collections of elements.

206. Calcium Oxid, CaO (Quicklime). *Preparation.* — Limestone is heated in a large furnace or kiln, carbon dioxid is driven off, and calcium oxid or quicklime remains in the furnace. $CaCO_3 = CaO + CO_2$.

Properties. — Lime is an amorphous, white, infusible solid. It has a strong affinity for water, combining with it to form the hydroxid or water-slaked lime with the evolution of much heat. Exposed to the air, it slowly absorbs moisture and carbon dioxid, and falls to a powder known as air-slaked lime, one of the forms of $CaCO_3$. When heated in the oxyhydrogen flame it gives forth an intense light of about 120 candle power, which is known as the calcium light.

Uses. — In making mortar and cement, in the calcium light, and for drying gases in the manufacture of illuminating gas, as well as in the laboratory.

207. Calcium Hydroxid, $Ca(OH)_2$. *Preparation.* — As stated above, by treating calcium oxid with about one-third of its weight of water.

Properties. — It is a white, alkaline, caustic powder, somewhat soluble in water, and having a strong affinity for carbon dioxid and hydrogen sulfid. It attacks animal tissues, as is shown by a plasterer's hand, and by its use in removing hair from hides in the tannery.

Uses. — Making mortar and whitewash, purifying gas, and in making brown sugar and glucose. Lime water is a solution of calcium hydroxid in water.

208. Calcium Carbonate, $CaCO_3$. *Occurrence.* — Calcite, chalk, marl, marble, Mexican onyx, and limestone are nearly pure calcium carbonate. It is the chief constituent of the shells of mollusks, corals, etc.

Properties. — It is sparingly soluble in water, but dissolves readily in water containing carbon dioxid, from which it is precipitated when the water loses its carbon dioxid. The formation of stalactites, stalagmites, travertin, etc., illustrate this property.

Uses. — Making quicklime, building, making glass, reducing iron ore, etc.

209. Calcium Chlorid, $CaCl_2$. — The properties of this substance are very different from those of the so-called "chlorid of lime." This salt is odorless, it deliquesces,* it has a strong affinity for water, and absorbs it from air or moist gases.

* Define term.

210. Calcium Chloro-hypochlorite, $Ca(OCl)Cl$. — This compound is extensively used in the arts under the name of bleaching powder, and is often wrongly called "chlorid of lime." It is prepared by treating slaked lime with chlorin. It is a white powder with an odor resembling hypochlorous acid. When treated with a strong acid it gives up all its chlorin. When treated with carbon dioxid it gives up hypochlorous acid. Exposed to the air, the carbon dioxid liberates the acid slowly, hence its action as a disinfectant.

211. Calcium Sulfate, $CaSO_4$, is found in nature as the mineral anhydrite, and in a hydrated condition as satin spar, alabaster, and selenite, which are different varieties of gypsum, $CaSO_4 + 2\ H_2O$. When slightly heated it loses its water of crystallization, and falls to a powder known as plaster of paris $(CaSO_4)_2H_2O$. This substance has a strong affinity for water, and when treated with it takes up the water of crystallization previously expelled, and hardens or "sets."

$$(CaSO_4)_2H_2O + 3\ H_2O = 2(CaSO_4 + 2\ H_2O).$$

Uses. — Gypsum is extensively used as a substitute for marble in buildings, as a fertilizer, and in the manufacture of plaster of paris. Plaster of paris is used as a cement; *e.g.* in incandescent lamps and in making casts.

212. Glass. — Ordinary window glass and bottle glass are silicates of calcium and sodium. In the manufacture of bottle glass somewhat impure materials may be used, and its green color is due to the presence of small quantities of the silicates of aluminum and iron. In window glass, as this green color is an objection, the purest materials obtainable are used. The color due to the small amount of iron which they contain is partially corrected by adding a small quantity of manganese dioxid. Bohemian glass, a silicate of potassium and calcium, has a higher melting point than

window glass, and on this account is largely used for chemical apparatus. Flint glass contains lead instead of calcium; it fuses easily, and is extensively used for optical instruments.

Glass Making. — At the Rochester glass works the following substances are melted for bottle glass: Clean sand, 100 lbs.; soda-ash, 40 lbs.; lime, 28 lbs.; feldspar, 1 lb. It requires from 12 to 14 hours to complete the melting.

Colored glass is made by adding a small quantity of a metallic oxid. Thus, cobalt colors glass blue; chromium, green; iron, green; gold, red; amber glass is made by adding soft coal.

Suggestion. — Write an essay on processes of melting, blowing, and annealing glass, making window glass, plate glass.

213. Mortar is made by mixing one part of lime with water to a thin paste, then adding three or four parts of coarse, sharp sand, and thoroughly incorporating these ingredients. When mortar is exposed to the air, calcium carbonate is slowly formed. Water is formed as the calcium hydroxid is transformed into the calcium carbonate.

$$CaH_2O_2 + CO_2 = CaCO_3 + H_2O.$$

This explains why plaster dries so slowly. The complete conversion of lime into carbonate requires a very long time, because the carbonate which is formed at first protects the rest. Rooms heated by open coke and charcoal fire dry more rapidly because the carbon dioxid which escapes into the room provides an abundant supply for the above reaction.

REVIEW QUESTIONS

1. Why does mortar harden?
2. Why is hair used in plaster?
3. Why not in bricklaying?
4. Why does plaster of paris set when treated with water?
5. What is mortar? What chemical action occurs when it hardens?

6. What is glass? How is it made?
7. How does Bohemian glass differ from window glass?
8. What will dissolve glass?
9. Describe the preparation of quicklime, writing the reaction.
10. Mention *two* important uses of calcium oxid.
11. Describe a lime-kiln.
12. Give the chemical names of plaster of Paris, marble, gypsum, and quicklime.
13. State the common names of calcium hydroxid and calcium chloro-hypochlorite.

CHAPTER XIX

SILVER, COPPER, AND GOLD

SILVER

SYMBOL AG. — ATOMIC WEIGHT 108

214. Occurrence. — Silver occurs uncombined in nature, but its most important ores are the sulfids and chlorids. Silver sulfid may be nearly always detected in the sulfids of other metals.

215. Properties. — Silver is a white metal permanent in air at ordinary temperature. Hydrogen sulfid acts readily upon it, forming a black coating of silver sulfid. It is the best conductor of heat and electricity known.

216. Extraction from its Ores. (*a*) *Pattinson process.* — Silver is extracted from ores consisting of mixed sulfids of lead, silver, etc., by the Pattinson process. The ore is roasted until the sulfur is expelled, and an alloy of silver and lead remains. This alloy is melted in large kettles and allowed to cool; the lead solidifies first and is dipped out. By this means a product is finally obtained which contains a high percentage of silver. This is heated in a stream of air, the lead oxidizes, and the silver remains; when all the lead has been removed, the silver reflects light, and the operator sees his face in the molten metal. This depends upon the fact that lead solidifies at higher temperature

than an alloy of lead and silver, and also upon the fact that lead oxidizes while silver is permanent.

(*b*) *Amalgamation process.* — Other ores of silver are reduced by the amalgamation process. The ore is thoroughly ground, mixed with common salt, and roasted, thus transforming all of the silver into a chlorid. The roasted mass is then placed in suitable vessels with water, iron scraps, and mercury, and vigorously agitated for many hours. The iron decomposes the chlorid, and the silver thus liberated forms an amalgam with the mercury. A portion of the mercury is removed by pressure, and the remainder by distillation, leaving the pure silver in the retort. The mercury is collected and used again.

217. Uses. — In jewellery, coins, etc., and in protecting other metals from the action of the air by electroplating.

218. Silver Nitrate, $AgNO_3$. — In contact with organic matter it turns black when exposed to the sunlight, hence it is a constituent of indelible inks. It corrodes the flesh, and is used by physicians to burn out wounds. It is sometimes called lunar caustic.

219. Photography. — The most important property of the salts of silver is their changing when exposed to light. The chlorids, bromids, and iodids are extensively used in photography. "A plate of glass is coated with the salt of silver, the plate is then exposed in a camera to light coming from the object to be photographed." The salt is changed where light strikes it, the amount of the change being proportionate to the intensity of the light. The image does not appear on the plate until after it is treated with a reducing agent, usually pyrogallic acid. After the image is

developed, the unchanged silver salt is dissolved off with sodium hyposulfite.

COPPER, Cu, 63.6

220. Occurrence. — Copper occurs native in large quantities near Lake Superior, in Chili, etc. In combination it is found as ruby copper, Cu_2O, as copper pyrites, a sulfid of iron and copper, and as a carbonate.

221. Preparation and Properties. — The oxid of copper is reduced by heating with charcoal. It is a hard reddish metal, having a metallic lustre. In moist air it becomes coated with a layer of carbonated copper. Copper forms two distinct series of compounds. There are two chlorids: cuprous chlorid, Cu_2Cl_2, and cupric chlorid, $CuCl_2$; also two sulfates, two oxides, etc. Copper sulfate, $CuSO_4 + 5\,H_2O$ (common name, blue vitriol), is largely used in galvanic batteries and in calico printing.

GOLD

Symbol Au. — Atomic Weight 197

222. Occurrence and Reduction. — This element is seldom found in combination in nature. In the parent ledges it occurs as isolated particles surrounded by quartz. As the ledge weathers, the particles of gold are carried down the streams with the quartz sand, forming placer deposits like those of the Klondike. At the ledge the rock is pulverized and carried over amalgamated copper plates by a stream of water. The gold forms an amalgam with the mercury, which is carefully removed and distilled. The gold of the placer deposits is recovered by mechanical washing.

223. Properties. — Gold is a soft, yellow metal, not affected by air or oxygen, even at high temperatures. It

is very malleable, easily beaten into sheets .0001 of a millimetre thick. When examined by transmitted light, these sheets appear green. It is very easily reduced; most metals precipitate it from solution, hence its use in toning photographs.

224. Uses. — Pure gold is too soft for use. Advantage is therefore taken of the fact that it forms alloys with copper and silver, either of which is more durable than pure gold. In Germany, France, and the United States the standard gold coin contains 90 % of gold and 10 % of copper. English gold pieces contain 11 parts of gold to 1 of copper. The metal with which gold is alloyed is easily recognized by the color of the alloy; that of copper having a reddish color, while that of silver is paler than pure gold. The fineness of gold jewellery is still expressed in carats. The *carat* is an old weight equal to the weight of four barleycorns, or $\frac{1}{24}$ of a Troy ounce. Jewellery is said to be 18 carats fine when a Troy ounce contains 18 carats of pure gold.

REVIEW QUESTIONS

1. Describe the process of extracting silver from its ores by amalgamation, giving chemical changes that take place.
2. Describe the process of photography, explaining the use of the compounds of silver employed.
3. State the common name, properties, and uses of silver nitrate.
4. From what acid was silver nitrate obtained?
5. State the properties of silver chlorid.
6. How does copper occur in nature? For what purposes is it used? Describe its most important compounds.
7. Discuss the occurrence of gold in nature.
8. Describe the extraction of gold from its ores, and state its principal uses.
9. Explain the blackening of silver spoons when in contact with boiled eggs.

CHAPTER XX

ZINC AND MERCURY

ZINC

SYMBOL Zn. — ATOMIC WEIGHT 65.4

225. Occurrence. — Zinc is said to have been found in Australia in the uncombined condition. In combination it is found as a carbonate, $ZnCO_3$ (calamin), as a sulfid, ZnS (zinc blende), as the red oxid, ZnO, and as a silicate.

226. Preparation. — The ores are first calcined, to reduce them to an oxid, and then mixed with charcoal and raised to a high temperature. The zinc oxid is reduced and the metal vaporized and condensed in iron vessels.

227. Properties. — Zinc is a bluish white metal, with a crystalline fracture; it melts at 412° C. and vaporizes at about 1000° C. It is exceedingly brittle, except between 100° and 150° C., when it is malleable, and may be rolled out into sheets. It is very soluble in acids, and burns in air with an intense blue light, forming zinc oxid, ZnO, a white flocculent substance formerly known as philosophers' wool. Zinc is permanent in air, because the coating of zinc oxid which forms when first exposed to the air prevents further oxidation.

228. Uses. — Zinc is extensively used in batteries and as a coating for other metals to protect them from the action

of the air. Galvanized iron is sheet iron coated with zinc, not by electricity, as the name would indicate, but by dipping the iron in molten zinc. Several important alloys contain zinc; *e.g.* brass, German silver, and the bronze used for coinage.

229. Principal Compounds. — Zinc oxid, ZnO, is a pure white substance, although it occurs native as the red zinc ore, its color being due to small amounts of manganese. It is often used as a substitute for white lead, because it is not blackened by hydrogen sulfid found in the air. Zinc chlorid, $ZnCl_2$, is a soft solid which may be distilled without decomposition. It has a strong affinity for water, absorbing it from the air, hence its use as a drier of gases. It is an excellent deodorizer, and is an important constituent of some of our best disinfectants. It is quite generally used by tinsmiths as a soldering fluid, as its aqueous solution dissolves the oxids which might prevent the adherence of the solder. It is also used to prevent timber from decay and to a limited extent as a caustic in surgery. When zinc oxid is moistened with zinc chlorid, a paste is formed which hardens quickly and is used in dentistry.

MERCURY

SYMBOL Hg. — ATOMIC WEIGHT 200

230. Occurrence and Preparation. — Mercury occurs free in nature, but the principal source from which it is obtained is cinnabar, a natural sulfid, which is found in California, Mexico, Peru, Spain, China, etc. Cinnabar is roasted and the vapor of mercury condensed in suitable vessels.

231. Properties. — Mercury is the only liquid metal. It has a silver-white color, hence its former name, quicksilver;

it freezes at $-39.5°$ C.; it volatilizes, and the vapor is 100 times as heavy as hydrogen. From this fact it appears that mercury is monatomic when a vapor. Mercury forms a soft alloy with most metals except iron. The alloys of mercury are called amalgams.

232. Uses. — Mercury is used in thermometers, barometers, pressure gauges, and other instruments. Chemists use it in collecting gases, and dentists use an amalgam of mercury and cadmium as a filling for teeth. In the arts it is extensively used in making mirrors and in the processes of extracting gold and silver from their ores. It is also used in voltaic cells.

233. Compounds. — Mercury forms two series of salts, the mercurous, like calomel, Hg_2Cl_2, and the nitrate, $Hg_2(NO_3)_2$, in which the double atom is bivalent; and the mercuric salts, like corrosive sublimate, $HgCl_2$, and the mercuric nitrate, $Hg(NO_3)_2$, in which the atom is bivalent.

REVIEW QUESTIONS

1. For what purpose is zinc chlorid used?
2. What is galvanized iron? Why is iron galvanized?
3. State the properties of zinc.
4. What important alloys contain zinc?
5. What are the chief ores of zinc?
6. Describe the physical properties of mercury.
7. Why is mercury used for thermometers? Barometers? What are the freezing and boiling points of mercury?
8. Describe the action of heat on mercuric oxid.
9. Mention some metals that will amalgamate with mercury.
10. What is cinnabar? How would you prove that it contains mercury?

CHAPTER XXI

ALUMINUM

Symbol Al. — Atomic Weight 27

234. Occurrence. — Aluminum is one of the most abundant elements. It is never found uncombined, but occurs in combination in most rocks and therefore in nearly all soil. Among the many common minerals which contain it are feldspar, mica, cryolite, corundum, and bauxite. Emery is an impure corundum. Several valuable gems contain aluminum. The ruby, sapphire, and oriental topaz are transparent crystals of corundum, Al_2O_3, the difference between them being due to the presence of small quantities of certain oxids. True topaz is a silicate of aluminum. The emerald is a double silicate of aluminum and berylium.

235. Reduction. — Until the invention of the electric furnace metallic aluminum was very expensive because metallic sodium was used in reducing it. Formerly it was worth $20 a pound, but now the price is about 40 cents. Most of the metal is now obtained from bauxite, Al_2O_3, H_2O, or from corundum, Al_2O_3. A wrought iron furnace is lined with carbon and partly filled with an artificial cryolite. Large carbon rods are thrust into the mass, and a powerful current sent from the rods through the mass to the furnace; the cryolite is melted, and dissolves the ore which is thrown in from time to time. The oxid is electrolyzed by the current, and metallic aluminum collects at the bottom of the furnace, while oxygen appears at the anode.

236. Properties. — Aluminum is a white lustrous metal, its color is between that of silver and that of zinc. It is very light (Sp. gr. 2.56, which is about one-quarter that of silver and about the same as that of glass). It is very malleable, is easily cast, is tenacious, and is more rigid than equal weights of other metals. It cannot be welded except by electricity. It is permanent in moist as well as dry air, even at moderately high temperatures. It melts at about 650° C., and is an excellent conductor of both heat and electricity. It is dissolved by hydrochloric acid and by solutions of sodium and potassium hydrates, but is not soluble in either sulfuric or nitric acids.

237. Uses. — The use of aluminum has rapidly increased within a year or so, and is now employed for many articles, from hairpins to horseshoes; from stove hollow ware to flying machines. Aluminum forms valuable alloys with copper and with steel; the most important of these is the aluminum bronze, which contains 90 % of copper and 10 % of aluminum. It has the color of gold, the tenacity of steel, takes a high polish, and does not tarnish in air.

238. Compounds. — Aluminum sulfate forms compounds with either sodium or potassium or ammonium sulfates, which belong to a class of double sulfates known as *alums*. All of the alums form beautiful cubical or octohedral crystals. Twenty-five different kinds are known, but only potassium alum, $KAl(SO_4)_2 + 12\ H_2O$, and ammonium alum, $NH_4Al(SO_4)_2 + 12\ H_2O$, are common. Alum is extensively used as a mordant by calico printers and dyers; it increases the amount of coloring matter which cotton cloth can absorb, and makes the color more permanent. Alum is often wrongly used as a constituent of cheap baking powder.

239. Hydraulic Cement, which is made by burning a limestone that contains aluminum silicate, owes its ability to set or harden when mixed with water to the formation of silicates of calcium and aluminum. As these silicates are insoluble in water, the cement may be used for submerged masonry.

240. Ordinary clay is an impure aluminum silicate; when mixed with water it forms a plastic mass which may be easily moulded into any desired shape, and which becomes hard, brittle, and very durable when dried and baked in a suitable furnace. The common clays are used in the manufacture of brick tile and earthenware.

Earthenware and tile are rendered impervious to water, or glazed, by throwing common salt into the furnace just before the "firing" is finished; the salt volatilizes, and forms a coating of sodium and aluminum silicate on the surface of the earthenware. The color of bricks and earthenware is largely due to the presence of iron oxids in the clay.

241. Porcelain clay or kaolin is a very pure silicate, $Al_4(SiO_4)_3H_2O$. In making porcelain a fine mixture of kaolin, feldspar, and quartz is employed. On strong ignition feldspar fuses, fills the pores of the clay, and thus furnishes a fused transparent mass. The finest porcelain is dried and heated to a red heat, forming a porous ware known as biscuit. This is dipped in water in which a small quantity of finely powdered feldspar is suspended. The article is now raised to a white heat, the feldspar increases the fusibility of the surface, and a thin, smooth, glassy coating results. The colors used in decorating are usually metallic oxids, and are almost always applied over the glaze in the better work.

REVIEW QUESTIONS

1. Discuss the physical and chemical properties of aluminum. Describe a process by which it may be extracted from some ore.

2. What is clay? How was it formed?

3. What is the chemical composition of alum?

4. Describe the metal aluminum. What name is given to its oxid?

5. What is hydraulic cement?

6. How does porcelain clay differ from the ordinary article?

7. State the occurrence in nature and uses of aluminum.

8. Mention the principal compounds of aluminum which occur in nature.

9. What is porcelain? How is it glazed?

10. State the uses of alum.

11. What advantage does aluminum possess over iron?

12. What alloys contain aluminum?

CHAPTER XXII

IRON

Symbol Fe. — Atomic Weight 56

242. Occurrence. — Iron is one of the most abundant as well as one of the most useful metals; it occurs uncombined in meteorites and in minute particles distributed through certain crystalline rocks. In combination with oxygen it occurs in enormous quantities in the older rocks, as magnitite, Fe_3O_4, which contains more than 72 % of iron; hematite, Fe_2O_3, with 70 % of iron; and as limonite, $2\ Fe_2O_3 + 3\ H_2O$, a hydroxid with about 60 % of iron.

Siderite, $FeCO_3$, is an important ore. Iron occurs as a sulfid known as pyrite, which is used in the manufacture of sulfuric acid, but which is not yet used as an ore. Most of the iron in this country is obtained from the oxids, but in England the principal source is "clay ironstone," a carbonate mixed with clay.

243. Extraction from its Ores. — If the ore is a carbonate or a hydroxid, it is calcined to expel the carbon dioxid or the water, and thus convert it into an oxid. The oxid is reduced by heating with carbon, usually a specially prepared coke made from soft coal. Charcoal is used in Sweden and Norway, where wood is plentiful. Most ores contain more or less silica and alumina, which must be converted into fusible silicates; to effect this, limestone is added to the mixture of ore and carbon, and a double silicate of calcium

and aluminum, a crude glass called slag, is formed. These reactions are brought about in a blast furnace (Fig. 17). It consists of a masonry tower some 80 feet in height and from 15 to 25 feet in diameter, lined with a most infusible fire-brick. Coke, limestone, and iron ore are introduced at the top in alternate layers by means of a cup and cone arrangement shown at *C*. A blast of hot air is forced through the furnace by powerful engines. The waste gases, which are carried off by the pipe *W*, are used to heat the blast to a temperature of about 600° C. In the hottest part of the furnace a temperature of about 1400° C. is probably reached. The iron is melted, and runs down to the bottom of the furnace at *I*. The melted slag being lighter floats upon it, and is drawn off at intervals through the slag hole. The crucible, as the lower part of the furnace is called, is opened three or four times a day and the iron allowed to run out into the sand moulds, forming bars three or four inches square and about four feet long, which are known as pig iron. When a furnace is in full blast charges are introduced at the top at regular intervals, and the process often continues uninterruptedly for years.

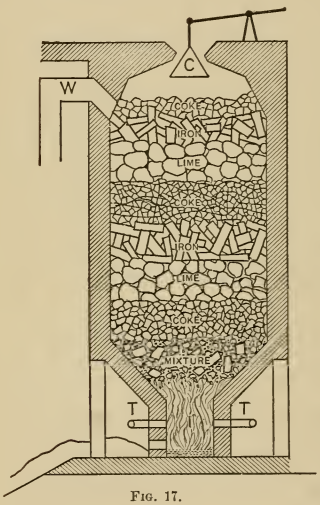


Fig. 17.

244. Pig Iron is brittle, crystalline, and easily fusible; it cannot be welded. It is not pure iron, but contains from 3 % to 6 % of carbon, and varying quantities of silicon, phosphorus, sulfur, and manganese. Most of the carbon is combined with the iron as a carbid, in what is known as *white cast iron*, whereas in *gray cast iron*, which is softer and more desirable for certain purposes, a large part of the carbon in the form of graphite crystals is mechanically disseminated through the iron. Sulfur and phosphorus are objectionable elements in iron, particularly if it is to be converted into wrought iron or steel; the sulfur makes it "hot short," that is, brittle when hot, and the phosphorus makes it "cold short," or brittle when cold.

245. Wrought Iron is tough, malleable, and fibrous in structure; it melts at 1500° C., and as it approaches this temperature becomes pasty, in which condition two bars may be firmly joined by hammering them together; it contains less than one-half of 1 % of carbon, cannot be tempered, and does not retain magnetism.

Preparation. — Wrought iron was originally prepared directly from the pure ore by heating it with charcoal and hammering the slag out of the mass; this process was known as "blooming." The process by which wrought iron is now prepared is termed "puddling." Cast iron is placed on the hearth (*H*) of a reverberatory furnace (Fig. 18), which is lined with a layer of ferric oxid. The iron is melted and constantly stirred to expose the impurity to the air; for a time the mass appears to boil, owing to the formation of carbon monoxid. As the impurities are oxidized, the mass becomes pasty, because of the higher melting point of wrought iron; and the pasty material is collected on one side of the furnace and worked up into

large lumps or blooms which are passed through rolls to remove the liquid slag. The ferric oxid used for the lining or *fettling* assists materially in oxidizing the impurities, and the process above described is sometimes called "pig boiling" to distinguish it from the "dry puddling" process in which the cast iron requires preliminary refining. For interesting history of wrought iron see Roscoe and Schorlemmer's *Chemistry*, Vol. II, pt. ii, p. 34.

246. Steel is malleable, has a fine crystalline structure, may receive a high polish, may be welded, is easily fusible, melting at about 1400° C. Its extensive use depends upon

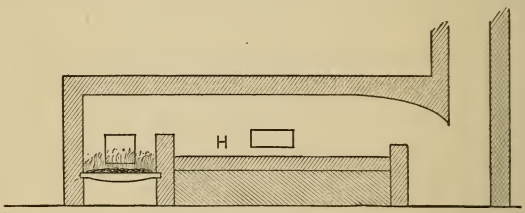


Fig. 18.

the fact that it may be tempered. When heated to redness and suddenly immersed in cold water, it is rendered very hard and brittle; if heated and slowly cooled, it is rendered soft, and by regulating the temperature at which it is tempered, almost any desired degree of hardness, toughness, or elasticity may be obtained. Steel contains from $\frac{1}{2}$ to 2 % of carbon.

Preparation. — Steel may be made in three ways: (*a*) by adding carbon to wrought iron (the cementation process), (*b*) by burning out a part of the carbon of cast iron (the Bessemer process), and (*c*) by melting together proper pro-

portions of wrought and cast iron (the Siemens-Martin process).

(*a*) *The Cementation Process.* — Bars of wrought iron are packed in charcoal in fire-clay boxes which are kept at a red heat for a week or more; the carbon penetrates the iron, giving it a blistered appearance, hence its name *blister steel.* It is not quite uniform in composition, but when remelted and cast into ingots this objection is overcome, and the *crucible steel* thus formed is considered the best kind for knives, springs, and tools; it is sometimes called cast steel.

(*b*) *The Bessemer Process.* — A large, covered, egg-shaped crucible, mounted on trunions, called a converter, and capable of holding from five to ten tons, is filled with melted cast iron. A powerful blast of air is blown through the converter, oxidizing the impurities; the peculiar flame of carbon monoxid is observed above the converter, and when this disappears, showing that the carbon has all been consumed, a definite quantity of *speigeleisen,* an iron rich in carbon, is added, and the mass is thus converted into the grade of steel desired. By this process a converter full of cast iron has been converted into steel in five minutes. This process has reduced the price to such an extent that some grades of steel are now sold at a lower price than wrought iron.

(*c*) *The Siemens-Martin Process.* — Pig iron is melted in an open hearth furnace, and wrought iron and iron ore are added in such quantities as to yield a product containing the desired percentage of carbon. Toward the close of the melting, which usually lasts eight or ten hours, a sample is taken and the percentage of carbon quickly determined by the chemist, who directs such changes in the mixture as may be necessary to produce the kind of steel desired.

247. Compounds of Iron. — Like mercury and copper, iron forms two series of salts corresponding to the two oxids with which the student is already familiar. For example, we have two chlorids, the ferrous, $FeCl_2$ and the ferric, Fe_2Cl_6, their properties being entirely distinct.

248. Compounds of Iron and Oxygen. — Iron forms three compounds with oxygen, viz.: —

Ferrous oxid,	FeO
Ferric oxid,	Fe_2O_3
Ferroso-ferric oxid,	Fe_3O_4

Ferrous oxid is a black powder which absorbs oxygen so rapidly that it takes fire when exposed to the air. When dissolved in acids it forms ferrous salts.

Ferric oxid is one of the important ores of iron. It is much used as a pigment in so-called iron paint. Jewellers' rouge, used in polishing plate glass and jewellery, is a finely ground, artificial ferric oxid; the red rust formed at ordinary temperatures is a hydrated ferric oxid, $2\,Fe_2O_3 + 3\,H_2O$, or a hydroxid, $Fe_2(HO)_6 + Fe_2O_3$, which absorbs oxygen from the air and communicates it to neighboring molecules of iron. We can now understand why iron does not rust in dry air at ordinary temperatures, and why the process proceeds so much more rapidly in moist air after an article becomes coated with rust.

Ferroso-ferric oxid is the richest of the ores of iron; it is attracted by a magnet (hence its common name, magnetite), and many specimens are strong natural magnets. The magnetic oxid, as it is often called, is formed when iron is raised to a high temperature in air. Unlike the hydrated ferric oxid, this oxid does not absorb oxygen from the air, but serves to protect a mass of iron from further rusting. Meteorites acquire a coating of this oxid which protects

them from the action of the air. In the Bower-Barff process of producing rustless iron for various ornaments, the articles are coated with magnetic oxid by heating them in superheated steam or in an oxidizing flame.

249. Compounds of Iron and Sulfur. — Four compounds of these elements are known.

Ferrous sulfid, FeS, is the most important to chemists, being a convenient and inexpensive source from which hydrogen sulfid can be obtained. It is a brittle, dark gray mass resembling a metal. It is prepared by dipping a white-hot wrought iron in melted sulfur, or by strongly heating a mixture of three parts of iron and two of sulfur. Exposed to the air, it slowly decomposes, forming sulfur dioxid and ferric oxid.

Ferric disulfid, FeS_2, occurs in nature as iron pyrite which is used by certain manufacturers in the process of preparing sulfuric acid.

Ferroso-ferric sulfid, Fe_3S_4, corresponds to the magnetic oxid of iron. It is attracted by a magnet, and some specimens are magnetic.

Iron sesquisulfid, Fe_2S_3, a fourth compound, is unimportant.

250. Sulfates. — Ferrous sulfate, $FeSO_4 + 7\ H_2O$ (green vitriol or copperas), is formed when iron is dissolved in sulfuric acid; it is usually manufactured by exposing heaps of iron pyrite to the action of the air and moisture at a gentle heat. Chemically pure ferrous sulfate forms transparent bluish green crystals which effloresce when exposed to dry air and become covered with a white incrustation. Ferric sulfate, $Fe_2(SO_4)_3$, resembles aluminum sulfate in that it combines with alkaline sulfates to form double sulfates or alums.

Ferrous sulfate is sometimes used as a disinfectant, but its chief use is in making black ink in connection with some astringent like tannic acid or nutgalls.

Experiment LXXXI. To prepare ink. — Dissolve $\frac{1}{2}$ gramme of tannic acid in 30 cc. of H_2O; to 22 cc. of this add a few drops of a solution of copperas and an equal amount of mucilage; a pale ink is formed which gradually darkens.

REVIEW QUESTIONS

1. Name the principal ores of iron.

2. Describe the manufacture of crucible steel, the manufacture of Bessemer steel, and state for what class of purposes each is used.

3. Distinguish chemically between pig iron and wrought iron. Describe the manufacture of each.

4. Describe three processes by which steel is made. Compare the cost of the processes and the value of the products.

5. Describe the manufacture of the following: (*a*) cast iron from ore; (*b*) wrought iron from cast iron; (*c*) steel from cast iron; (*d*) steel from wrought iron.

6. How does ferrous sulfate differ from ferrous sulfid? From what acid was each obtained, and for what is each used?

CHAPTER XXIII

TIN AND LEAD

TIN

Symbol Sn. — Atomic Weight 119

251. Occurrence. — Although tin is not widely diffused in nature, it occurs in very large quantities in a few localities, viz. in Cornwall, England, and in Saxony. It has recently been discovered in South Dakota. It is probable that tin does not occur free in nature, although it is reported that metallic tin is found in Siberia and Guiana. Tin stone or cassiterite, SnO_2, is the only ore that is now reduced.

252. Reduction. — The finely crushed ore is washed free from earthy matter, then calcined in a reverberatory furnace to expel certain impurities and oxidize others, then washed a second time. The ore thus purified is mixed with powdered anthracite coal, and again heated in the furnace.

253. Properties.

Experiment LXXXII. — Examine pieces of tin and lead, noting the color, lustre, and hardness of each. Compare the freshly cut surface of each with a surface that has been exposed to the air for some time. Which metal is the better as a coating to prevent oxidation of other metals? Which is the more easily oxidized? Which metal is the more malleable? Brittle? Elastic? Has either metal a crystalline structure? (To answer this dip a piece of each metal in dilute aqua regia.)

At ordinary temperatures tin is easily beaten into sheets known as tin foil. At 200° C. it is brittle and may be powdered, and at 228° C. it melts. The crystalline structure

of tin is often brought out for purposes of ornamentation. When a bar of tin is bent, the surfaces of the crystals within the bar rub against each other, making a peculiar creaking sound known as the "tin cry," and a perceptible increase in temperature at the point of flexure may be caused by bending a bar backwards and forwards a few times. Ordinary tin plate, or in common parlance, tin, is thin sheet iron coated with a film of tin by dipping it in a bath of the molten metal. A cheaper variety, called terne plate, used for roofing, and sometimes for cheaper tinware, is coated with an alloy of tin and lead. Such ware should never be used for cooking or for making cans for preserving fruits and vegetables, because the acids of the foods may form poisonous compounds with the lead.

254. Alloys. — Tin forms a large number of useful alloys.

Pewter contains three parts of tin to one of lead.

Britannia metal contains tin 84 parts, antimony 10 parts, copper 4 parts, and bismuth 2 parts.

Soft solder contains equal parts of tin and lead.

Bell metal and *bronze* are alloys of copper and tin, and the "fusible metals," some of which will melt in boiling water, are usually alloys of tin, bismuth, lead, etc.

Among the important alloys which do not contain tin, the following may be mentioned: Brass contains 1 part copper and 2 parts zinc; German silver is brass whitened with nickel; coin silver is silver with 8 to 10 parts of copper; gold coin consists of gold with 8 to 10 parts of coin silver; aluminum bronze contains aluminum 9 parts and copper 1 part. All alloys melt at a lower temperature than that of either constituent.

255. Compounds. — Tin forms two series of compounds: the stannic, in which the atom is quadrivalent, and the

stannous, in which it is bivalent. Beside the stannic oxid, SnO_2, which occurs in nature, stannous oxid, SnO, is known; it is a black substance soluble in acids, forming stannous salts. The best known compounds of tin are the chlorids. Stannous, $SnCl_2$, is an excellent reducing agent, and is used by dyers. The tin salt of commerce is a crystalline stannous chlorid, $SnCl_2 + H_2O$. Stannic chlorid, $SnCl_4$, is also used by dyers. Stannic sulfid, SnS_2, is a golden yellow crystalline substance, and is largely used as a pigment under the name of mosaic gold.

LEAD

Symbol Pb. — Atomic Weight 207

256. Occurrence. — The few specimens of metallic lead which have been found free in nature were probably formed by the reduction of ores of lead by volcanic action. In combination it occurs in enormous quantities; the most abundant compounds are the sulfid, PbS, known as galenite, and the carbonate, $PbCO_3$, known as cerussite. The sulfate and the chlorid also occur in considerable quantities. Nearly all the lead of commerce is obtained from the sulfid. Small quantities of the sulfid are found in New York State, in the Niagara limestone.

257. Reduction. — Lead is easily reduced from its ores. It was one of the seven original metals of the ancients. The richer ores are heated to a dull red heat on the hearth of a reverberatory furnace. Sulfur dioxid is given off, and there remains a mixture of lead oxid, lead sulfate, and lead sulfid. The air is now shut off and the temperature raised, converting the above compounds into metallic lead and sulfur dioxid. About 10% of the lead remains in the furnace, mixed with the slag; this may be recovered by

the process described below. The poorer ores are heated in a small cupola or blast furnace, with coke and metallic iron or ferrous silicate. Iron sulfate is formed, the lead is reduced and is drawn off at the bottom of the furnace.

258. Properties and Uses.

Experiment LXXXIII. — Grind a little oxid of lead with a few cubic centimetres of water in a mortar, filter, and test for lead with hydrogen sulfid. Is lead oxid soluble? Is lead suitable for pipes in which to convey drinking water?

All soluble salts of lead are poisonous. Write a brief account of the properties of lead shown by Experiment 78.

Lead is extensively used for water pipes, for plates of storage batteries, in making shot, in preparing white lead, and in various alloys.

259. Compounds. — Lead forms five oxids having the following formulas: Pb_2O, PbO, Pb_2O_3, Pb_3O_4, PbO_2. Of these, litharge, PbO, and red lead, Pb_3O_4, are the most important. Red lead is extensively used as a pigment, and in the manufacture of flint glass for lenses, cut glassware, etc. The dioxid, PbO_2, a chocolate colored powder, is an excellent oxidizing agent. It is formed on the positive electrode of a storage battery during charging. *White lead,* which forms the basis of most paints, is a basic carbonate, having the formula $2\,PbCO_3$, $Pb(OH)_2$. *Lead chromate,* $PbCrO_4$, commonly known as chrome yellow, is also used as a pigment.

REVIEW QUESTIONS

1. Describe the physical properties of lead.
2. What are the chief ores of lead?
3. What compounds of lead are used as pigments?
4. What are the chief properties of tin?
5. What is tin plate? What are its advantages over iron plate? Over Terne plate?
6. From what ores is tin obtained?

CHAPTER XXIV

PLATINUM

SYMBOL Pt. — ATOMIC WEIGHT 194.9

260. Occurrence. — Platinum is invariably found uncombined in nature, and is usually associated with the related metals, osmium, iridium, paladium, etc. Most of the platinum of commerce is obtained from the Ural Mountains, but small quantities are found in California, Australia, and Brazil.

261. Preparation. — The ore is treated with aqua regia, which does not dissolve osmium and iridium; the solution is treated with ammonium chlorid, which precipitates a double chlorid of ammonium and platinum. This is ignited, driving the chlorin and ammonium off, and leaving a spongy mass known as platinum sponge.

262. Properties.

Experiment LXXXIV. — Examine a piece of platinum, noting its color, malleability, and specific gravity. Heat a piece in the Bunsen burner. Does it melt? Is it oxidized in the flame? Endeavor to fuse a bit of platinum wire into a glass tube; try other kinds of wire. Why is platinum used in incandescent lamps? Is it soluble in any of the ordinary acids? Save any salts formed.

263. Uses. — The properties shown above make platinum a very useful article to the chemist; platinum wire, foil, crucibles, and various other utensils are in constant use in every laboratory. Its permanence in air leads to its use for small weights, and it is exclusively used in incandescent lamps and other apparatus in which an electric current is to be conducted through glass.

PART II

CHAPTER XXV

CARBON

Symbol C. — Atomic Weight 12

264. **Occurrence.** — This important element occurs free in nature in each of its three allotropic forms, viz. the diamond, graphite, and charcoal; combined with oxygen as carbon dioxid, it occurs in the atmosphere and in many mineral waters, also in limestone, marble, and all carbonates. All living things contain carbon. In the animal kingdom it is usually combined with hydrogen, oxygen, and nitrogen, and in the vegetable kingdom with hydrogen and oxygen.

The number of carbon compounds formed in the life processes of plants and animals is almost infinite, and it was once believed that these compounds could not be formed in any other way, that they possessed some peculiarity of molecular structure due to the action of vital force, and, therefore, could not be prepared by laboratory processes; these compounds were distinguished as *organic* substances, and those which could be prepared without the aid of vital force were called *inorganic* substances. There is now no good reason for maintaining this distinction except the great number of compounds and the similarity of their properties. It is quite likely, however, that for these reasons the terms

"organic chemistry" and "inorganic chemistry" will be retained, but the old meaning is gone; and now organic chemistry may be defined as *the chemistry of the carbon compounds.*

265. The Diamond. — Diamonds are found in the East Indies, Brazil, Mexico, Australia, Africa, Borneo, and Sumatra. There is some evidence that diamonds exist in other celestial bodies, as they have been recently found in meteors. The diamond is the hardest substance known, and can be ground and polished only with its own dust. When polished it has a magnificent lustre, and its high refractive power causes it to sparkle and show varied colors, although the gem itself is generally colorless. Its beauty and rarity make it the most precious of gems (the Regent diamond is valued at $ 500,000). If heated to a high temperature, it swells up and is converted into a substance resembling graphite, which burns, forming carbon dioxid. In 1814, Sir Humphry Davy proved that carbon dioxid was the only product of the combustion of a diamond, thus proving that it was pure carbon.

Uses. — It is used as a gem; by the glazier in cutting glass; in the diamond drill for boring rocks and other hard substances. Its powder is used in grinding and polishing gems of all kinds.

266. Graphite is familiar as the "black lead" of the misnamed "lead pencil." It is found abundantly in nature, large beds occurring at Ticonderoga, N.Y., and famous ones in Siberia and on the island of Ceylon. It occurs both in the crystalline and amorphous forms, but its crystals are not the same shape as those of the diamond. Ordinary coke or charcoal is converted into graphite when heated in the

arc light. About a quarter of an inch of the end of a carbon from an electric lamp is always an impure graphite. Considerable graphite has been formed as a by-product in the process of making carborundum in an electric furnace, and a company has now been formed to manufacture graphite by the Acheson process, in which powdered graphite mixed with certain oxids is passed in a continuous stream through an electric furnace, which converts it into a high grade of graphite. The inventor believes that the coke first combines with the metal of the oxid, forming a carbid, and that as the temperature rises, the carbid is decomposed and the metal volatilized, leaving a pure graphite.

Properties. — Graphite is opaque, has a grayish color and a metallic lustre; it is very friable, is quite soft, leaving a mark on paper, hence its name; it is insoluble in all known liquids, is a good conductor of both heat and electricity, and is smooth and slippery to the touch. It is permanent in air at ordinary temperatures, but burns, forming carbon dioxid, when raised to a high temperature.

Uses. — Graphite is used in making lead pencils and crucibles for molten metals, as a lubricant, as stove polish, for foundery facings (to secure smooth castings), in the process of electrotyping, and in paint.

267. Amorphous Carbon. — The amorphous varieties of carbon are almost always obtained by charring some organic substance, *i.e.* by burning it in a limited supply of air. The hydrogen and the volatile compounds are burned, leaving the amorphous carbon. The principal varieties of amorphous carbon are charcoal, lampblack, gas carbon, and animal charcoal.

268. Charcoal. — The ancient way of "coaling wood," as the process is still called, is carried on as follows: In the

centre of a carefully levelled piece of ground, termed the "hearth" or "earth," a centre pole is erected, and around this the wood is piled, forming a flattened cone. This is covered with earth, the centre pole is withdrawn, leaving a "chimney," at the bottom of which the fire is kindled. During the early stage of the process much smoke and flame formed by the combustion of the volatile matter issues from the top of the pile. As soon as this disappears, all vents are closed and the mass allowed to cool. In this process there is great liability to loss through the admission of too much air, and the by-products are all wasted.

Retort Charcoal. — In this process the wood is heated in retorts from which air is excluded, thus preventing combustion of the charcoal. The liquids driven off, consisting of tar, pyroligeneous acid, wood alcohol, acetone, benzol, etc., are collected in suitable condensers, and the gases liberated, which consist mainly of marsh gas, hydrogen, carbon monoxid, and acetylene, are used in heating the retort; small wood and sawdust can be charred by this method.

269. Properties of Charcoal.

Experiment LXXXV. — Carefully measure and weigh a small piece of dry pine, place it in a test tube and cover it with dry sand; apply heat as long as gas is evolved. Is the gas combustible? When the evolution of gas ceases, set the tube aside to cool; empty the tube and examine the sand. Is there any evidence that either of the liquid products was retained by the sand? Which? Measure and weigh the charcoal. How do the linear dimensions compare with those of the wood used? How does the volume compare? Examine with a glass to determine whether the grain of the wood is preserved. Twist a small wire about a piece of charcoal and hold it in the Bunsen burner flame until ignited; does it melt? does it burn with a flame? Why does wood burn with a flame? Is charcoal soluble in acids? in alkalies?

Experiment LXXXVI. Filters. — Place about a teaspoonful of animal charcoal in a test bottle; fill the bottle nearly full with a

solution of potassium permanganate ; shake the bottle vigorously, then pour the contents on a filter. What is the color of the liquid ? What property does charcoal possess that renders it useful in filters ?

Experiment LXXXVII. Charcoal as a Deodorizer. — Into the neck of a funnel thrust a bit of cotton and cover it to a depth of two or three centimetres with powdered charcoal ; through this filter pass a quantity of water charged with hydrogen sulfid, and observe.

Experiment LXXXVIII. Carbon as a Reducing Agent. — 1. Mix two or three grammes powdered copper oxid, CuO, and about $\frac{1}{10}$ its weight of powdered charcoal ; heat in an ignition tube fitted with an outlet tube. Pass the gas which is given off into clear lime-water contained in a test tube. What is the appearance of the substance left in the tube ? Does it suggest the metal copper ?

2. Treat a little with strong nitric acid. What should take place if the substance were metallic copper ? (Refer to process of making nitric oxid.) What does take place ? What is the reaction which takes place between the copper oxid and the charcoal ? Write the equation.

Experiment LXXXIX. Products of the Combustion of Carbon. — Twist a bit of wire about a small piece of charcoal, hold it in the flame of a Bunsen burner until it is well ignited, then insert it in a test bottle containing a little lime-water. Cover the bottle with the hand for a minute, remove the charcoal, and shake the bottle. What occurs ? What compound is formed by the combustion of charcoal ?

Experiment XC. (Performed by Teacher.) — Collect a bottle of ammonia gas over mercury. Heat two or three lumps of charcoal to redness and pass them through the mercury into the ammonia. What occurs ? Estimate the relative volumes of the charcoal and the gas.

Experiment XCI. Does Charcoal Float ? — Drop a piece of charcoal in a glass of water and place the glass under the receiver of the air pump. Exhaust the air. Explain.

At ordinary temperatures the chemical energy of charcoal is exceedingly feeble. It is, therefore, one of the most durable of substances. It is frequently found in prehistoric fireplaces in a very perfect state of preservation. The charred grain found in the excavations at Pompeii is as fresh as if burned yesterday. The charcoal carbonized at about 300° is a soft, brownish black substance igniting at about

380°, while that carbonized at high temperatures is dense and difficult to ignite. The absorption and condensation of gases by charcoal is due to so-called surface action, *i.e.* to the adhesion between the molecules of the gas and the charcoal. It is probable that in the case of the easily liquefiable gases a portion of the gas is condensed to the liquid state by this action (a phenomenon which should increase the temperature of the carbon).

The condensed gases manifest marked chemical activity, for example, hydrogen and chlorin combine even in the dark when absorbed, and absorbed hydrogen sulfid is so rapidly oxidized when charcoal containing it is placed in oxygen as to ignite the charcoal. This property explains the action of charcoal as a disinfectant. The atmospheric oxygen which is condensed in the pores of the charcoal oxidizes the offensive and injurious gases. Charcoal has been known to absorb 170 volumes of dry ammonia.

Uses. — The amorphous varieties of carbon are extensively used as reducing agents as in the processes of smelting, in which ores are reduced to metals by heating them with some form of carbon and in the Leblanc process. Charcoal is used in filters, as a disinfectant, and for kindling purposes.

270. Lampblack.

Experiment XCII. — Close the holes at the base of a Bunsen burner, and hold a piece of cold metal in the flame. Examine the deposit of lampblack formed. Describe it.

On a large scale lampblack is prepared by burning substances rich in carbon in a limited supply of air. The dense smoke formed passes through chambers in which coarse blankets are suspended, and on these the soot collects.

Uses. — Great quantities of lampblack are used in the manufacture of printer's ink, paints, and electric light carbons.

271. Animal Charcoal. — Boneblack, as this substance is sometimes called, is prepared by carbonizing bones in iron retorts. It contains about 10 % of carbon, but it possesses many of the valuable properties of charcoal in a marked degree, because the carbon is disseminated throughout the porous mass of calcium phosphate, which forms about 88 % of the mass.

Uses. — Sugar refiners use animal charcoal filters to clarify solutions of raw sugar, and oil refiners also use it to decolorize the better grades of lubricating oils.

272. Relative Kindling Temperature of Carbon and Hydrogen. — The kindling temperature of hydrogen is probably between 500 and 600° C., and that of carbon is very much higher. One of the results of this difference in kindling temperature was seen in Experiment 92, in which the flame of a fuel composed of hydrogen and carbon was cooled below the kindling temperature of carbon, and the carbon was no longer consumed, a part of it was deposited on the metal, and the balance escaped as smoke. All smoky flames may be attributed to the fact that the temperature of a portion, or possibly the whole of the flame, is below the kindling temperature of carbon; and the smoke would disappear or would be "consumed" if the temperature of the flame should be raised so that all parts should be above the kindling temperature of carbon.

A second effect of this difference in kindling temperature is shown in the facility with which certain fuels may be kindled. When a fuel containing carbon and hydrogen is to be kindled, it is only necessary to supply sufficient heat to raise it to the temperature at which it evolves hydrogen, or some compound of hydrogen and carbon, and to kindle the evolved gas; whereas if the fuel is a pure carbon it must be

raised to a much higher temperature before it "takes fire." This explains the ease with which wood or soft coal is kindled as compared with hard coal or coke.

In the process of making water gas it is found that at the high temperature of the anthracite fire, carbon manifests sufficient energy to take oxygen away from hydrogen, whereas we now find that at certain lower temperatures hydrogen combines with oxygen and carbon does not. Few better illustrations of the effect of heat upon chemical energy have been suggested.

273. Smoky Flames. — The temperature attained by a flame depends upon the rate at which the fuel is consumed, and upon the rate at which the heat escapes.

As already illustrated in several processes, the rate of combustion of fuel may be controlled by regulating the amount of air supplied; when too little air is supplied the flame is cooled, and this is one of the chief causes of smoky flames.

As has already been shown, smoky flames are sometimes due to chilling the flame by contact with cold objects. If the cold object is a good conductor of heat, the effect continues a longer time, as is noticed when one builds a fire in a cold stove.

A third cause of smoky flame is the presence of moisture in the fuel, a large amount of heat is withdrawn from the flame to vaporize the moisture, thus lowering the temperature. To this cause the great volume of smoke noticed when green wood or grass is burning is due.

274. The Instability of Organic Substances. — A number of causes combine to make organic compounds less stable as a rule than inorganic compounds.

(*a*) The chief cause undoubtedly lies in the fact that carbon compounds are subject to the attacks of micro-organisms. To this cause we must attribute all cases of putrefaction and decay. Both animals and plants require carbon, and their food is principally composed of substances containing carbon, but certain carbon compounds, like carbolic acid and some of the organic poisons, are not attacked by microörganisms.

(*b*) Some of the most unstable of the organic compounds owe their instability to the presence of nitrogen. The feeble affinity which characterizes the nitrogen atom renders the decomposition of the substance containing it less difficult than it would be if some more active element replaced the nitrogen; hence most animal products are unstable.

(*c*) All organic compounds are endothermic; and endothermic substances are less stable than exothermic, because they do not require the expenditure of energy to effect their decomposition.

(*d*) The elements found in organic compounds differ widely in valence; carbon is quadrivalent, oxygen is bivalent, nitrogen trivalent, and hydrogen univalent, thus rendering a greater number of combinations possible than could be formed if they were all of the same valence. We thus have many organic compounds of the same elements which are easily changed into kindred forms.

(*e*) The molecules of many organic compounds are exceedingly complex, sometimes containing more than 100 atoms, united in various sub-groups, or radicals, to form the molecule. The energy required to bring about a rearrangement of these radicals in the molecule, or the elimination of one or more radicals, is less than that required to decompose simpler molecules, and they are therefore less stable.

275. Use of Organic Substances as Fuels. — All organic things are endothermic, *i.e.* they develop heat when they combine with oxygen. The quantity of heat developed by the oxidation of carbon and hydrogen is greater than that developed by any other elements, and for this reason organic substances are particularly valuable as fuels. Another decided advantage lies in the fact that the products of the combustion are in the aeriform state when formed, and are therefore easily carried away by the draft of the chimney.

REVIEW QUESTIONS

1. Why do we char fence posts and telegraph poles?

2. Show why lamp chimneys are used. Why is gas flame spread out like a bat's wing?

3. Why is air introduced in the centre of the flame of the "Rochester burner"?

4. Why is more smoke seen to issue from a chimney on starting a fire than after it has burned for a time?

5. Why is a curling iron blackened when held in the gas flame?

6. Discuss the chemical energy of charcoal.

7. Describe an experiment to demonstrate that the diamond is a form of carbon.

8. Compare the charring of wood by fire with the charring of wood by acid.

9. In what respects are charcoal filters better than other kinds for purifying drinking water? If a porous stone or porcelain filter is used, what may be done to attain the same end as that attained by the use of the charcoal filter?

10. Discuss the use and care of a charcoal filter as compared with the use and care of some other filter.

11. How does charring of wood protect the wood from decay? How does charging wood with creosote affect its liability to decay?

12. Show why utensils used over a wood fire are generally more blackened than those used over a coal fire.

13. Can you build a bonfire of anthracite coal as you build one of dry wood? Give reason for your answer.

14. What causes a fire to smoke? State two methods employed to overcome this difficulty.

15. From what country does the graphite used in Faber pencils come? in Dixon pencils? (Consult legend on pencil.)

16. What can you say of the affinity of charcoal for oxygen at high temperatures? How does it compare with the affinity of other substances for oxygen at high temperatures?

17. Discuss the shrinkage of wood when carbonized.

18. Describe and explain the combustion of charcoal.

19. Does turning a lamp wick up affect the air supply? Why does raising the lamp wick cause the lamp to smoke?

20. Explain why wood is ignited at a lower temperature than coal.

CHAPTER XXVI

CARBON AND OXYGEN

SECTION I. — CARBON DIOXID

FORMULA CO_2. — MOLECULAR WEIGHT 44

276. Occurrence. — This gas is a constant constituent of the atmosphere, to which it is supplied by the respiration of animals, and by combustion and decay. It is found in all spring waters, and issues from the earth in many places. The Poison Valley in Java and the Grotto del Cane near Naples owe their properties to the carbon dioxid, which is supplied from subterranean sources. Old wells are frequently filled with it.

In combination with bases, carbon dioxid occurs in large quantities; *e.g.* limestone, marble, etc.

277. Preparation.

Experiment XCIII. To prepare carbon dioxid, and to determine certain of its properties; (*a*) *color*, (*b*) *odor and taste*, (*c*) *weight*, (*d*) *solubility*, (*e*) *combustibility.* — In the generating bottle place eight or ten lumps of marble or chalk (not prepared crayons). Cover the lumps with water, and add a small quantity of hydrochloric acid. Collect several bottles of the gas by downward displacement.

1. Lower a lighted taper into a bottle of the gas, and observe. Now introduce a burning stick into the same bottle.

2. Place a lighted taper in an empty bottle, and pour the contents of the second bottle of gas upon the flame, proceeding as if pouring water.

3. Pour some of the gas into a bottle containing lime-water; shake the bottle; this is the test for carbon dioxid.

4. Prove that the gas may be transferred by pouring from one vessel to another.

5. Is carbon dioxid soluble in water? Explain the results obtained, and state the properties of carbon dioxid illustrated by each section of the experiment. Complete the following reaction: —

$$CaCO_3 + 2\,HCl = CO_2 +$$

Experiment XCIV. — Object: *To determine what acids, if any, will decompose carbonates. The test for carbonates.* — 1. Place as much sodium acid carbonate as you can take up on the blade of a penknife in a test tube. Arrange a short delivery tube.

2. Cover the carbonate with dilute sulfuric acid.

3. If a gas is evolved, pass it through lime-water. What is it?

4. Repeat the experiment, using (*a*) hydrochloric acid; (*b*) acetic; (*c*) any weaker acid. Which acids decompose carbonates? What substances evolve carbon dioxid when treated with an acid?

Experiment XCV. Object: *To investigate the direct combination of carbon dioxid with bases.* — 1. Fill a test bottle one-fourth full of a solution of sodium hydroxid.

2. Pass carbon dioxid through the solution as long as it is absorbed.

3. Add acid to a portion of the solution.

4. Devise a test which will prove what gas is evolved.

5. Write the reactions which occur when the gas is passed through the solution, and when the acid is added.

Experiment XCVI. Object: *To determine why lime-water is rendered turbid by carbon dioxid.* — 1. Collect some of the white insoluble substance formed by passing carbon dioxid through lime-water on a filter.

2. Treat the white precipitate with dilute acid. What evidence have you that it is calcium carbonate? How was the carbonate formed?

278. Physical Properties. — Your experiments have shown you the color, odor, taste, solubility, and weight of this gas. At ordinary temperatures and pressure, water dissolves about its own volume of carbon dioxid. As pressure is increased, the solubility increases; this fact is illustrated in the ordinary aerated waters. Water under a pressure of several atmospheres is saturated with the gas, and when the pressure is reduced to one atmosphere by withdrawing

the cork, or by drawing a glassful from a fountain, the excess of gas dissolved at the higher pressure is liberated, causing the familiar effervescence. At $-5°$ C. carbon dioxid is liquefied by a pressure of about 31 atmospheres; under ordinary pressures it boils at $-87°$ C. It is a colorless, mobile liquid, which floats on water without mixing with it.

Liquid carbon dioxid is prepared on a large scale by compressing the gas evolved in the process of brewing, in steel cylinders; in this form it is largely used by manufacturers of aerated waters. When liquid carbon dioxid is allowed to escape into air, the absorption of heat due to rapid evaporation causes a portion of the liquid to solidify. The solid carbon dioxid is a soft, white, snow-like substance. It is now an article of commerce known as carbonic acid snow.

279. Chemical Properties. — The solution of carbon dioxid in water is feebly acid, and may be regarded as the true carbonic acid. $CO_2 + H_2O = H_2CO_3$. That all carbon dioxid dissolved in water is not chemically combined with it is shown by the fact that a freshly prepared sample of aerated water effervesces more briskly than those that have long been preserved. Thus Apollinaris water, when opened, effervesces very little, while when gently heated it gives off a rapid stream of gas. Such waters have in all probability been exposed to pressure for a long time, and the dissolved carbon dioxid has almost entirely combined to form carbonic acid.

In the test for carbon dioxid (Experiment 93) the turbidity was due to the formation of the insoluble calcium carbonate.

$$CaH_2O_2 + CO_2 = CaCO_3 + H_2O.$$

Let us repeat this experiment to illustrate another property of carbon dioxid.

Experiment XCVII. — Pour a small quantity of lime-water into a test tube; pass carbon dioxid through it for some minutes. Does the turbidity increase at first? Does it continue to increase, or is a point reached where all the calcium is converted into calcium carbonate? Continue the supply of carbon dioxid until the liquid becomes clear. Now expel the excess of carbon dioxid by boiling the liquid. What occurs? Is calcium carbonate soluble in water containing carbon dioxid? If still in doubt, pass carbon dioxid through some water, and pour it into a test tube containing calcium carbonate prepared as above.

The fact that water containing carbon dioxid will dissolve calcium carbonate accounts for the hardness of natural waters in limestone regions, and also for the formation of caves in limestone; and the precipitation of the dissolved calcium carbonate, when the carbon dioxid is given off, causes the formation of the so-called scale in tea-kettles and steam boilers, the formation of stalactites and stalagmites in caves, and the deposits of petrified moss, or travertine, near certain springs.

280. Why Carbon Dioxid does not support Combustion. — Although carbon dioxid contains more than three times as much oxygen as the air, it does not support ordinary combustion, for it is itself a product of combustion, and as should be inferred from the chemical energy manifested when carbon dioxid is formed, the elements have a strong affinity for each other. Metallic potassium, sodium, and magnesium are among the few elements which have a sufficiently strong affinity for oxygen to take it from carbon, and at high temperatures carbon dioxid supports the combustion of these substances.

Experiment XCVIII. — Light a strip of magnesium ribbon, and thrust it into a bottle of carbon dioxid. Describe the action. What becomes of the carbon of the CO_2? Test a small piece of the substance into which the ribbon is converted with dilute hydrochloric acid to determine whether it is an oxid or a carbonate. Write the reaction.

The efficiency of the fire extinguisher and the "chemical" fire engines depends upon the fact that carbon dioxid does not support combustion. These devices consist of two receptacles, a larger containing a solution of sodium acid carbonate, and the smaller a few ounces of sulfuric acid. The receptacles are usually so arranged that the liquids may be mixed by inverting the extinguisher. Carbon dioxid is generated, and water charged with the gas is forced out, extinguishing any moderate conflagration.

281. Growth. — One of the broad differences between living and dead matter is in the manner of growing. All living organisms grow because of the multiplication of cells *within* the body of the organism; while inert matter is either subject to disintegration, or as in the case of the crystal, grows by the addition of similar molecules to the *outside*. The growth of the plant differs from that of the animal, in that plants constantly increase in bulk by addition to their store of organic matter, while animals expend a large percentage of the material which they receive in replacing the tissues worn out by the activities of life.

Experiment XCIX. To determine what gas plants evolve. — 1. Place a growing plant in a shallow vessel and cover it with a stoppered bell jar.

2. Pour enough water into the vessel to prevent the escape of gas from the bell jar, and fill the bell jar with carbon dioxid.

3. Set the apparatus in the sunlight for a few hours.

4. Test the gas in the jar for carbon dioxid by lowering a lighted taper into it. Is the taper extinguished? Has anything replaced the carbon dioxid? If so, what?

5. Repeat the experiment, having air instead of carbon dioxid in the bell jar, and covering it with a heavy cloth or otherwise excluding all light.

6. After a few hours test the air in the jar for carbon dioxid by dipping out a bottle full and testing it with lime-water, also by lowering a lighted taper into the jar. Explain any change that you note in

composition of the air. What gas is absorbed by plants in the light? In the dark? What gas is evolved in each case?

282. The Life Processes of Plants and Animals. — Plants live on inorganic substances, chiefly carbon dioxid, water, ammonia, and salts; the carbon dioxid is absorbed from the air by the leaves, and the other substances are derived from the soil. The carbon dioxid and water are reduced by the action of sunlight, and the carbon and hydrogen thus liberated combine with oxygen to form starch, $C_6H_{10}O_5$, with a reaction which is perhaps expressed by the following equation: —

$$6\,CO_2 + 5\,H_2O = C_6H_{10}O_5 + 12\,O.$$

There can be no doubt that the chemical energy which effects the decomposition of the carbon dioxid is derived from the sunlight; and it is equally certain that chlorophyll, the green coloring matter of the plant, is necessary to the reaction, but the part played by the chlorophyll is not known. The twelve atoms of oxygen liberated by the formation of one molecule of starch are returned to the air.

Animals are unable to produce the complex organic matter required to renew their bodies; they therefore depend either directly or indirectly upon plants for their food. In the animal body this organic matter is oxidized and exhaled as carbon dioxid and water, a process which maintains the high temperature of the animal. It thus appears that the heat as well as the energy possessed by an animal is developed by the combustion of portions of his own body by means of oxygen supplied to the air by plants, and that the material consumed can only be renewed by foods produced by plants.

The process of respiration in both plants and animals consists in the absorption of oxygen from the air, the *oxida-*

tion of portions of their tissues, and the release of carbon dioxid and water. The process is the opposite of assimilation, in which plants reduce carbon dioxid and exhale oxygen; but it occurs at all times, even at daylight, when it is overshadowed by assimilation. The quantity of carbon dioxid evolved in twenty-four hours by the respiration of a given plant is only a small fraction of that assimilated by the plant in the same time.

283. Purification of the Air. — Careful analyses of such samples of bottled ancient air as have been found fail to show an appreciable difference between the air which the ancients breathed and that of to-day. The vegetable kingdom has been able to reduce the carbon dioxid poured into the air by the oxidation of thousands of tons of animal matter and by the combustion of thousands of tons of fuel, and to return to the air practically all of the oxygen taken from it.

This reciprocal relation of the life processes of plants and animals may be nicely illustrated in a small way by supplying an aquarium with such proportion of plants and animals that the amount of oxygen evolved by the plants shall just equal the amount absorbed by the animals, thus rendering the renewal of the water unnecessary. Although this action of plants is the only means of supplying oxygen to the air, it is not the only means employed by nature to keep the composition of the air constant and to remove harmful impurities therefrom.

During the colder months of the year, when the quantity of carbon dioxid received by the air is greater than at any other time because of the increased consumption of fuel, the action of plants in this latitude is practically suspended, and the amount of carbon dioxid in the air would increase

were it not for the action of the winds and for the tendency toward equal distribution of gases known as the property of diffusion. The rain is an important agent in the removal of impurities, dissolving carbon dioxid, nitric acid, ammonia, and all soluble substances; and washing down germs, dust, soot, and organic matter exhaled by animals.

Sunlight also destroys germs, and to a certain extent prevents the pollution of the air by drying up damp places or stagnant pools.

284. Ventilation. — The putrid organic matter exhaled from the lungs and discharged through the pores of animals is much more harmful than the carbon dioxid which accompanies it; still the amount of carbon dioxid in the air may be taken as an index of the impurity of the air, for the two substances are given off by the lungs in proportional quantities. It is a well-established fact that air which is contaminated by the products of respiration acts as a poison to those who breathe it, but the subject of ventilation has not yet received the study which its importance demands, and our knowledge of the subject is in a somewhat chaotic state. The most that can be said at present is, good ventilation requires an *inlet* for fresh air, an *outlet* for impure air, and some means of setting the air in motion. In cases of "natural" ventilation, or those in which no special appliance is employed to cause the circulation of the air, let the outlet be at the upper part of the room; but no system of natural ventilation has yet been devised which can be depended upon in all conditions of wind and weather. The system of artificial ventilation which gives most satisfactory results requires some mechanical means of forcing the air through the rooms.

SECTION II. — CARBON MONOXID

SYMBOL CO. — MOLECULAR WEIGHT 28

CAUTION. — Do not inhale this gas.

285. Preparation.

Experiment C. — In a large Florence flask place 3 grammes of finely powdered potassium ferrocynid and 25 grammes of strong sulfuric acid. Heat gently over wire gauze; remove the burner as soon as gas is evolved rapidly. Collect two bottles over water.

1. Test the inflammability of the gas.
2. Thrust a lighted splinter into the gas and observe.
3. When the gas is pure, remove the delivery tube from the flask and connect the bent glass tube in its place and ignite the gas as it flows from the tube; observe the characteristics of the flame.
4. Hold a cold dry bottle over the burning jet.
5. Pour a little lime-water into the bottle and shake it. What is the product of the combustion? Is water formed? Why?

State the physical properties of carbon monoxid. Note the character of its flame.

Experiment CI. — Pass a stream of carbon dioxid through a tube containing red-hot charcoal, and from this lead the gas through a bottle containing caustic soda. Collect the gas over water; ignite a bottle of the gas. What is it?

This experiment illustrates the method by which carbon monoxid is formed in coal stoves. The carbon dioxid formed by the combustion of the lower layers of coal passes through the hot coal above and is reduced to carbon monoxid, which burns with the characteristic blue flame when it comes in contact with the air above the coal.

286. Physical Properties. — Carbon monoxid is very sparingly soluble in water, and may be collected over water with very little loss. It may be liquefied, but with very great difficulty. It is very poisonous. When inhaled it combines with the hæmoglobin, forming a bright red compound which cannot collect and distribute oxygen; less than one per cent

of carbon monoxid in the atmosphere gives rise to headaches and giddiness, and if inhaled for any considerable time, insensibility and death quickly follow. The extremely poisonous nature of the "choke damp" resulting from a colliery explosion is due to the presence of carbon monoxid with the carbon dioxid formed as a product of the combustion. A pan of smouldering charcoal gives off this gas, and in certain countries is a frequent means of suicide.

As carbon monoxid is odorless, coal gas could not be detected in the air were it not that carbon monoxid is usually accompanied by other gases having peculiar odors. Carbon monoxid is an important constituent of water gas. The chief objection to the use of water gas for the illumination of dwellings arose from the fact that while the water gas was more poisonous than the ordinary illuminating gas, it was odorless, and therefore leaks could not be detected except by the illness of persons. This objection has been overcome by adding to water gas certain gases which have partly an odor, and which increase the light.

287. Chemical Properties. — At high temperatures carbon monoxid has a strong affinity for oxygen, and is an excellent reducing agent; it forms an explosive mixture with air and with oxygen, which is the cause of the explosions which sometimes occur in coal stoves.

288. Heat and Chemical Energy of the Combustion of Carbon. — The heat developed by the combustion of a gramme of carbon is about 8080 calories; something less than $\frac{1}{4}$ as much as is developed by the combustion of an equal weight of hydrogen, but a larger amount than is developed by the combustion of any other element.

It is an interesting fact that the two elements yielding the largest quantities of heat are the ones recovered from

the products of combustion by plants. We have here a species of endless chain; the fuel supply of the world can never be entirely exhausted. All fuels contain either carbon or hydrogen, and most of them contain both.

289. Application of this Energy in doing Mechanical Work. — The steam engine is to-day our main reliance for power; it may be considered as a machine which converts the chemical energy of fuel into heat, and the heat in turn into mechanical motion. The chemical energy of carbon

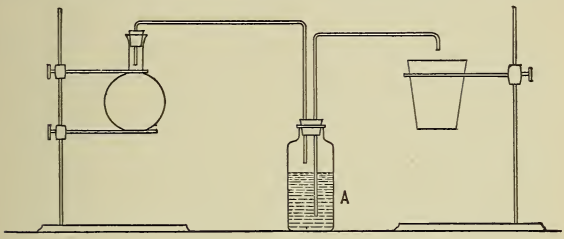


Fig. 19.

is the principal source from which our power is derived, but it is not the only source; hydrogen forms some 20% of the weight of certain coals, and therefore supplies more than half of the heat units developed. The work done by explosives is derived directly from chemical energy without passing through the intermediate form.

Experiment CII. To illustrate the transformation of the chemical energy into mechanical motion. — 1. Arrange apparatus as in sketch, the flask being empty.

2. The bottle *A* is $\frac{3}{4}$ full of water.

3. Heat the flask with Bunsen burner. Why does water rise? What chemical energy is used in this experiment? In what other forms does it appear?

Experiment CIII. To illustrate the direct transformation of chemical energy into mechanical motion. — 1. Remove the flask and tube

leading to bottle *A* (Experiment 98). Close the hole in the rubber stopper.

2. Refill the bottle and see that the tumbler is empty.

3. Mix 3 grammes of sodium bicarbonate and an equal weight of tartaric acid.

4. Raise the stopper of the bottle and pour the mixture into it. Describe and explain.

The action is similar to that of the fire extinguisher, in which sulfuric acid is used instead of the tartaric acid used in this experiment.

SECTION III. — A STUDY OF FLAME

290. We have studied a number of cases of combustion, some of which developed flames, while others burned without flame. It will assist us to understand the cause of this difference in behavior, if we divide the combustible substances which we have studied into two classes. (*a*) Those which burn with flame, such as hydrogen, water gas, sulfur, phosphorus, hydrogen sulfid, carbon monoxid, wood, rosin, kerosene, alcohol, paraffin, illuminating gas. (*b*) Those which burn without flame, as charcoal, iron, copper. Do all the gases mentioned above burn with flame? All the liquids? All the solids? Are the substances which burn without a flame volatilized easily or with difficulty?

Experiment CIV. To examine the structure of the flame produced by the combustion of a hydrocarbon. — 1. Examine the flame of a candle, noting: (*a*) the blue cup-shaped portion, (*b*) the dark space, (*c*) the luminous cone, and (*d*) the thin layer. (To see the latter hold the candle near a blackboard. If this does not make it clear, hold flame in the sunlight and examine the shadow cast on white paper.)

2. Make a sketch of the flame in your note-book, indicating the parts.

Experiment CV. To determine which portion of the flame is hottest. — Lower a piece of cardboard into the candle flame until it nearly touches the wick; hold it in place until it begins to char on the upper side, then quickly remove it to prevent its taking fire. What portion of the flame is hottest? Preserve this cardboard in your note-

book. This shows a cross-section of the flame. To secure a longitudinal section hold a card horizontally, with one edge touching the wick below the flame; revolve the card about the edge in contact with the wick until it is vertical. As soon as the side away from the flame begins to turn brown remove the card. Examine the section of the flame shown on the card. What portion of the flame is evidently hottest? Coolest? Is there any relation between the temperature and the intensity of the light of the various parts of the flame?

Experiment CVI. — 1. Spread the wick of the candle to make the flame as large as possible.

2. Pass a match stick through the flame just above the wick, hold it there a few seconds, remove it, and quickly blow it out.

3. Describe the charred portion of the match. Is the dark portion of the flame a zone of combustion?

Experiment CVII. Alternate. — 1. Thrust the head of a match into the dark portion of the candle flame. Hold it there while you count ten rapidly. Is it ignited while in the dark portion, or as it is withdrawn?

Experiment CVIII. To determine the state of the matter forming the dark portion of the flame. — 1. Hold a burning match stick two inches above the wick of a burning candle; blow out the candle flame. What occurs when a stream of "smoke" which rises from the hot wick returns to a vertical position and comes into the match flame? Is this "smoke" combustible?

2. Again extinguish the flame and hold a piece of filter paper in the stream of "smoke"; after the smoke ceases examine the paper for evidence that the stream consisted of either solids or liquids.

3. Relight the candle, hold a gas tube, drawn out to a point at one end, in the dark zone the pointed end upward; hold a lighted match at the upper end. What is the state of the matter in the dark zone? Explain how the paraffin reaches the flame; also the changes of state which it undergoes. Is the candle flame due to the combustion of a solid, a liquid, or a gas?

Experiment CIX. To determine why certain flames are luminous.— 1. Adjust the supply of gas so that the Bunsen flame is non-luminous.

2. Sprinkle a very little powered charcoal in the flame; how is the amount of light affected?

3. Sprinkle reduced iron in the flame.

4. Rub two pieces of charcoal together near the orifices at the base

of the burner. How is the amount of light affected? Explain how the charcoal reaches the flame.

5. Make a spiral by winding a short piece of iron wire about a lead pencil; hold this in the upper part of the flame; how is the light affected? How did the solids placed in the oxyhydrogen flame affect the amount of light?

6. Hold the mantle of a Welsbach burner in the flame.

7. Close the holes at the base of the Bunsen burner; note the changes in the amount of light. Hold a piece of glass tubing in the flame for a short time. Examine the tube for evidence that any element existed in the flame in a solid state.

8. Open the holes in the base of the burner; scrape some of the deposit from the glass tube, holding the tube near the openings at the base of the burner. How is the amount of light affected? Explain. What is your opinion as to the cause of the light produced by burning hydrocarbons?

Experiment CX. The Bunsen Burner.—1. Examine the construction of a Bunsen burner. Make a sketch showing its parts.

2. Describe the parts of a Bunsen burner flame. If necessary use the shadow.

3. Explore the flame with a piece of platinum wire to determine in what zone or part of a zone the highest temperature is reached. (Judge by the degree of incandescence of the wire.)

There is good authority for the statement that the luminosity of certain flames is due to the presence of vapors of sufficient density to become incandescent at the temperature of the flame, and it is probable that the luminosity of gas and candle flames is due to this cause acting conjointly with the presence of solid matter.

291. Oxidizing and Reducing Flames.—In the outer portion of the candle flame and the Bunsen flame there is an excess of oxygen, hence substances heated in this portion of the flame are oxidized. In the inner portion of each of these flames there is a deficiency of oxygen, and substances containing oxygen are reduced when in this portion. The mouth blowpipe is usually used to increase the efficiency

of these flames. With a little practice one learns to close the opening between the mouth and nasal passages, and to force air through the blowpipe by contracting the cheek muscles, breathing regularly through the nose meanwhile. In this way one may blow a steady stream of air into a flame for several minutes. The tip (*b*) of the outer flame is the most efficient oxidizing flame, and the tip (*a*) of the inner cone, the most efficient reducing flame.

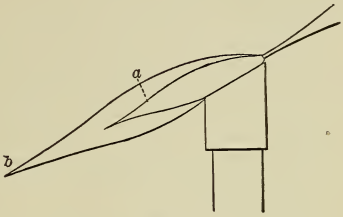


FIG. 20.

Experiment CXI. To reduce lead oxid. — 1. In a hollow made in a piece of charcoal place a small quantity of lead oxid, PbO.

2. Using a blowpipe, heat it in the reducing flame until a metallic globule is obtained.

3. Compare the physical properties of the globule with those of lead.

Experiment CXII. To oxidize lead. — 1. Place a small piece of lead in a hollow made in a piece of charcoal.

2. Heat the lead in the oxidizing flame. In what previous experiment was the coating formed on the charcoal obtained? What is the substance?

REVIEW QUESTIONS

1. Mention seven physical facts concerning carbon dioxid.
2. What are carbonates? How may they be detected?
3. Describe fully the formation of "fur" in the tea-kettle.
4. What is the great supporter of vegetable life? animal life?
5. What binary compounds are present in limestone? How would you separate these binary compounds, and how would you cause them to combine again?
6. Describe an experiment in which chemical energy ultimately performs mechanical work.

7. Compare the physical properties of carbon monoxid and carbon dioxid as follows: state, color, odor, and taste, solubility, weight, difficulty of liquefaction, and solidification, effect of pressure on solubility. Compare the chemical properties of carbon monoxid and carbon dioxid as follows: combustibility, relation to animal life, to vegetable life, stability.

8. Account for the unpleasant and sometimes dangerous explosions that frequently occur in coal stoves shortly after fuel is added.

9. Carbon dioxid is nearly $\frac{3}{4}$ oxygen, while air is only $\frac{1}{5}$ oxygen. Why is a flame extinguished in the former, and supported in the latter?

10. Compare the respiration of animals with that of plants.

11. Show how hæmoglobin and chlorophyll are of use to animals and plants respectively.

12. Explain in detail the conditions of light and heat in the flame of a Bunsen lamp when the holes in the base of the lamp are (*a*) open, (*b*) closed.

13. In household chemistry how is carbon monoxid formed?

14. State two reasons why organic substances are usually more suitable as fuels than inorganic substances.

15. Are the life processes of animals essentially processes of oxidation or of reduction?

16. Is the process of assimilation by plants a process of oxidation, or reduction?

17. Why does not the air of cities become overcharged with carbon dioxid? How is carbon dioxid absorbed at the poles? in the winter?

CHAPTER XXVII

HYDROCARBONS

292. The binary compounds of hydrogen and carbon are known as hydrocarbons. Chemists are familiar with between one and two hundred of them, and thousands more are theoretically possible. They all form oxids, hydroxids, etc., which are known as hydrocarbon derivatives, and which are so numerous that a list of their names would fill a good-sized volume. Fortunately, very simple relations exist between the chemical compositions and between the properties of the members of several large groups or series; and the study of these compounds is therefore greatly simplified. For example, the paraffin or the marsh gas series is based upon the compound CH_4, and the first six members of the series have the following formula: —

Methane,	CH_4,	Butane,	C_4H_{10},
Ethane,	C_2H_6,	Pentane,	C_5H_{12},
Propane,	C_3H_8,	Hexane,	C_6H_{14}.

It will be seen that each formula differs from the preceding by CH_2 and that each may be expressed by the general formula C_nH_{2n+2}.

We shall study very briefly the three following substances: —

Methane, CH_4, basis of the C_nH_{2n+2} series.
Ethene, C_2H_4, basis of the C_nH_{2n} series.
Acetylene, C_2H_2, basis of the C_nH_{2n-2} series.

METHANE

(MARSH GAS. FIRE DAMP)

FORMULA CH_4. — MOLECULAR WEIGHT 16

293. Occurrence. — Marsh gas is found free in nature in large quantities. It is formed by the decay of vegetable matter in a limited supply of air. As the name indicates, it is found in marshes; the bubbles which rise to the surface, when the mud at the bottom of the pond is disturbed, are largely marsh gas. It is one of the products of the process of reduction by which coal was formed, and exists, often under great pressure, in seams and crevices in the coal beds. Petroleum contains it; it often forms a large percentage of "natural gas" and is present in illuminating gas to the extent of 35 or 40 %.

294. Preparation.

Experiment CXIII. — 1. Mix 2 grammes of fused sodium acetate, $NaC_2H_3O_2$, 4 grammes of caustic soda, and 5 grammes of quicklime. Reduce the mixture to a fine powder.

2. Heat the mixture on a piece of sheet iron until all moisture is expelled.

3. Charge a long ignition tube with the mixture, support it horizontally, and apply heat; collect the evolved gas over water in small bottles. Note its physical properties.

4. Thrust a lighted taper into a bottle of marsh gas. Describe the flame as to light and heat. What are the probable products of its combustion? How can you prove that your answer is correct? Test the bottle for carbon dioxid. Do you note any evidence of the formation of water?

5. Determine whether the gas supports combustion.

6. Determine whether it is heavier or lighter than air.

Quicklime is used in this experiment to make the mass porous, and is not changed chemically. The reaction is as follows: —

$$NaC_2H_3O_2 + NaOH = CH_4 + Na_2CO_3.$$

QUESTIONS

Why does this gas explode when mixed with the air and ignited? In what proportion should the mixture explode with most violence? Why do miners call this gas fire damp?

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O.$$

If the above equation expresses the reaction which occurs when marsh gas explodes, how should the volume of the factors compare with that of the products (Avogadro's law)? What effect should the heat developed by the combustion have upon the relative volumes?

Which of the products in the above reaction is known as choke damp and why is this name given it?

295. Uses. — Natural gas, which is largely marsh gas, is used extensively as fuel in various manufacturing establishments and in households.

296. Marsh Gas in Coal Mines. — The violent explosions which frequently occur in coal mines are due to the ignition of an explosive mixture of fire damp and air. When fire damp explodes the products of its oxidation fill the mine; one of these products is known as choke damp. To prevent these explosions care is taken to thoroughly ventilate the mines, and miners' lamps (Fig. 21) are usually enclosed in wire gauze so that the flame cannot pass through the gauze and ignite the gas outside of the lamp.

Fig. 21.

ETHENE

(ETHYLENE. OLEFIANT GAS)

Formula C_2H_4. — Molecular Weight 28

297. Occurrence. — Ethene is one of the important constituents of illuminating gas, of which it forms from 4 to 10 %.

298. Preparation.

Experiment CXIV. (Performed by teacher.) — In a large flask mix cautiously 80 cc. of sulfuric acid and 20 cc. of alcohol (C_2H_6O). Apply gentle heat and collect the gas evolved over water. Is the gas heavier or lighter than air? Is it soluble in water? Ignite a bottle of the gas and force the gas out by pouring water into the bottle. Describe the characteristics of the flame. What compounds are formed? From an inspection of the formulæ, CH_4 and C_2H_4, would you expect the difference observed in the flames of marsh and olefiant gases? Explain.

The principal reaction which occurs in this experiment is expressed in the following equation: —

$$C_2H_6O = H_2O + C_2H_4.$$

The strong affinity of sulfuric acid for water, withdraws hydrogen and oxygen from the alcohol in the proportion which they unite to form water. The gas thus prepared contains several impurities, which may be removed by passing through strong sulfuric acid and then through sodium hydroxid.

299. Properties. — Mixed with three volumes of oxygen and ignited, ethene explodes violently. Explain. It burns with a dull, smoky flame, when mixed with two volumes of chlorin and ignited, forming HCl and C. Ethene may be liquefied at 0° C. by a pressure of 41 atmospheres. When the liquefied gas is rapidly evaporated, the extremely low temperature of −140° C. may be obtained. Liquid ethene is therefore used in the liquefaction of oxygen and other gases requiring very low temperatures.

ETHINE
(ACETYLENE)

FORMULA C_2H_2. — MOLECULAR WEIGHT 26

300. Acetylene is formed when coal gas is burned in an insufficient supply of air. Its peculiar odor may be de-

tected when the flame of the Bunsen burner "snaps back"; *i.e.* when the gas is ignited at the bottom of the burner.

301. Preparation.

Experiment CXV. — 1. Drop a small piece of calcium carbid, CaC_2, into a tin cup that is about half full of water; ignite the escaping gas. Describe its odor, flame.

2. Hold a small piece of calcium carbid with tongs, drop a *few drops* of water on it, ignite; then try to extinguish the flame with a miniature fire extinguisher made as in Experiment 99.

Experiment CXVI. — 1. Place a small piece of calcium carbid, CaC_2, under the mouth of a bottle arranged in the water pan for collecting a gas over water.

2. Observe any change in the volume of the gas. Is it soluble in water? What is its color?

3. Determine whether the gas is heavier or lighter than the air. Of the three hydrocarbons prepared, which produces the brightest light? Does the brilliancy of the light produced depend upon the proportion of carbon in the compound? Of the three, which requires the most oxygen for its complete combustion?

$$CaC_2 + 2\,H_2O = CaH_2O_2 + C_2H_2.$$

302. Properties. — Acetylene is poisonous. It explodes violently under conditions which have not been well understood. At present, however, it seems to be established that the gas may be safely handled if the pressure under which it is confined does not much exceed one atmosphere. At a temperature of $+10°$ C. it is liquefied by a pressure of 63 atmospheres. The deep red color obtained when acetylene is passed through a solution of cuprous chlorid in ammonia water is a very sensitive test for this gas.

303. Derivatives. — Among the more important oxygen derivatives of the several homologous series of hydrocarbons are the hydroxids, the oxids, and the acids. The hydroxids are known as *alcohols*, and are formed by replacing one of the hydrogen atoms of some hydrocarbon with

the radical, OH. The best known examples are methyl hydroxid, or wood alcohol, CH_3OH, and ethyl hydroxid, or ordinary alcohol, C_2H_5OH. The alcohols have distinct basic properties, and combine readily with the various acids, forming *ethereal salts.* The oxids are known as *ethers,* the best known example being ordinary ether, or ethyl oxid $(C_2H_5)_2O$. The *acids* formed by the further oxidation of the hydrocarbons form an interesting group; they combine with the inorganic bases, as well as with the alcohols, to form salts. In the following list the names and formulæ of six members of the series of acids derived from the marsh gas series of hydrocarbons are given: —

Formic acid,	CH_2O_2,	or $H.CO.OH$.
Acetic acid,	$C_2H_4O_2$,	or $CH_3.CO.OH$.
Propionic acid,	$C_3H_6O_2$,	or $C_2H_5.CO.OH$.
Butyric acid,	$C_4H_8O_2$,	or $C_3H_7.CO.OH$.
Palmitic acid,	$C_{16}H_{32}O_2$,	or $C_{15}H_{31}.CO.OH$.
Stearic acid,	$C_{18}H_{36}O_2$,	or $C_{17}H_{35}.CO.OH$.

These acids are commonly known as the *fatty acids,* because they occur abundantly in most natural fats; butyric acid is found in butter, palmitic acid in palm oil, and stearic acid in stearin. The so-called stearin candles are a mixture of palmitic and stearic *acids.* The *fats,* in a natural state, are ethereal salts formed by the union of the fatty acids with glycerin, a tribasic alcohol derived from propane, having the formula $C_3H_5(OH)_3$.

304. Soaps. — Like metallic salts, the ethereal salts are decomposed when treated with an alkaline hydroxid. The ethereal salts usually require a higher temperature to bring about the reaction, but all of them are decomposed when boiled with sodium or potassium hydroxid, the products of

the reaction being a salt of the alkalin base and an alcohol. As this sort of decomposition occurs in the process of making soap, it is called *saponification*. When a fat, as glycerin palmitate, for example, is boiled with sodium hydroxid, sodium palmitate (a soap) and glycerin are formed; the reaction may be expressed as follows: —

$$C_3H_5(C_{16}H_{31}O_2)_3 + 3\,NaOH = 3\,NaC_{16}H_{31}O_2 + C_3H_5(OH)_3.$$

Ordinary soaps are usually palmitate or stearate of potassium or sodium. The sodium salts make *hard soaps*, and the potassium salts, *soft soaps*. The detergent or cleansing power of soap depends upon the fact that its solution either dissolves, or forms an emulsion of oily substances that water alone would have no effect upon.

Experiment CXVII. To make soap. — 1. Dissolve one part of sodium hydroxid in eight parts of water.

2. Mix 50 cc. of the above solution with 50 cc. of castor oil and boil for half an hour.

3. Add 200 cc. of water and bring to a boil.

4. Add 20 grammes of common salt. The soap separates and solidifies as the liquid cools.

REVIEW QUESTIONS

1. Describe the artificial preparation of marsh gas, and state its properties, its use, and the manner of its occurrence in nature.

2. Account for the presence of CH_4 in coal mines. Why is it dangerous? What precautions should be taken to avoid this danger?

3. Distinguish between fire damp and choke damp, giving the chemical name, formula, and properties of each.

4. Describe the preparation of acetylene, writing the reaction. State one important use of acetylene.

5. Compare the physical properties of methane, ethene, and ethine; the chemical properties.

6. Describe the manufacture of soap; write the reaction.

7. What are soaps? State the theory of the use of soaps in cleansing.

8. Describe the manufacture of hard soap.

CHAPTER XXVIII

DESTRUCTIVE DISTILLATION

305. Distillation. — The term *distillation* is applied to a number of operations which differ among themselves in many important respects, but in all of which a substance is heated and a vapor given off which is condensed in a cooled receiver. Two varieties of distillation depend only upon physical changes. The first variety, which might be called *simple physical distillation*, was illustrated by Experiment 43, in which water was separated from dissolved solids. The second variety is known as *fractional distillation*, and is employed in separating liquids. If a mixture of water and ether be heated in a still, it begins to boil when slightly above the boiling point of ether, 35°, and the ether vapor accompanied by the small amount of water vapor, due to the normal evaporation of water at this temperature, is condensed. As the proportion of ether in the mixture is diminished the boiling point rises, and the proportion of water vapor condensed increases, so that it is customary to collect the distillate in separate portions or fractions of the whole, hence the name. By repeated distillation of the "fractions" two or more liquids may be quite completely separated by this process.

There are also two classes of distillation which involve chemical changes. The first of these was illustrated by Experiment 51, in which a chemical change was brought

about by means of a reagent and the applied heat. As the temperature reached is sufficient to vaporize one of the products of the chemical change, it is easily separated from the other products by condensation. This is *simple chemical distillation.*

In the remaining class, which is known as *destructive or dry distillation,* a chemical change is brought about by heat alone, the absence of reagents being an essential condition. In the many important applications of this process in the arts, the substance distilled consists of animal or vegetable matter; and when such substances are heated in a retort from which air is excluded, the products of their decomposition are quite different from the products of their combustion. Those products which are volatile may be separated by passing the vapors through a succession of condensers which are kept at different temperatures.

The second method of preparing charcoal, the process of manufacturing coal gas, and process of preparing animal-charcoal or bone black are processes of destructive distillation. Coal, petroleum, and natural gas were formed by the destructive distillation of organic matter under ground.

306. Illuminating Gas. — There are two kinds of illuminating gas in common use, — coal gas, and the so-called water gas. Coal gas is generally prepared by the destructive distillation of bituminous coal, although wood, resin, or petroleum may be used. The coal is placed in fire-clay retorts which are heated by a coke fire. A vertical pipe connects each retort with a large horizontal pipe called the hydraulic main. When the coal is heated, the volatile products pass through the "riser" into the hydraulic main. Here the temperature of the gas is lowered somewhat by contact

with the metal of the pipe, and some of the water vapor, tar, and ammonia salts are condensed. From the hydraulic main the gas flows through several hundred feet of pipe called the "condenser." The pipe is exposed to the air and is designed to cool the gas and condense the liquid products of the distillation. Tar, benzol, tuluol, water, and ammonia salts are collected here; and the mixture, called the ammoniacal liquor, is drawn off into cisterns. From the condenser the gas passes through a "scrubber," where it is washed. The scrubber is a large iron tank, frequently six or eight feet in diameter and twenty feet high, filled with coke, blocks of wood, or scraps of tin, the object being to expose a large surface to the gas. A spray of water is introduced at the top of the scrubber, and the material filling it is thus kept moist. The remainder of the tar and ammonia salts are here removed, and the gas passes on to the purifier. This is a large rectangular box, frequently twenty feet square and four feet deep, and is filled with layers of quicklime which absorbs water, carbon dioxid, and hydrogen sulfid. The gas passes through successive purifiers until a test shows that all the above substances have been removed. It then passes to the gas holders and is ready for the consumers. Of the products of distillation of bituminous coal, one is solid, viz. coke, which is found in the retort; four are liquid, viz. tar, benzol, tuluol, and water containing a variety of ammonia salts in solution; eight are gases, viz. hydrogen, nitrogen, marsh gas, olefiant gas, acetylene, carbon monoxid, carbon dioxid, and hydrogen sulfid. It seems likely that a small amount of the vapors of benzol and tuluol are also present in the gas and that they increase the illuminating power. The gas delivered to the consumer is a mixture of all the above gases except hydrogen sulfid and carbon dioxid.

Experiment CXVIII. (For two students.) *To prepare coal gas.* — 1. Fill a gas-pipe retort* 6 inches long, one-fourth full of pieces of dry pine wood; support it so that it may be strongly heated.

2. Connect two bottles so that the gas evolved shall bubble through the liquids which they contain.

3. The first bottle should be two-thirds full of cold water, the second one-third full of lime-water. From the second bottle lead the gas to the water pan, collect two bottles of the pure gas; then substitute a tube drawn out to a point for the delivery tube in the water pan and ignite the gas. Describe the flame. When the flow of gas ceases, examine the bottle of lime-water. Of what two substances do you find chemical evidence here? Examine the first bottle for evidences of ammonia, tar, and oil. Open the retort and examine the coke.

Experiment CXIX. Examination of Illuminating Gas. — 1. Hold a strip of filter paper moistened with a solution of lead acetate, in a stream of gas coming from the Bunsen burner. (See Art. 170.) What substance is detected by this test?

2. Hold a strip of moistened red litmus paper in a stream of the gas. The presence or absence of what impurity is indicated by this test?

3. Pass a stream of the gas through a bottle of lime-water. What impurities have you found in the gas tested? What is your conclusion concerning the efficiency of the purifiers at the gas works furnishing the gas tested?

307. Coke. — Large quantities of coke are now made from the fine coal or slack which was formerly considered valueless and which accumulated rapidly about coal mines. Bituminous coal, containing between 20% and 30% of volatile hydrocarbons, melts when burned or when heated in a retort, and on cooling leaves a hard porous mass having a metallic lustre. The slack is thoroughly washed

* Obtain of the plumber a $\frac{3}{4}$ inch nipple 6 inches long, a $\frac{3}{4}$ cap, a $\frac{3}{4}$ to $\frac{1}{4}$ reducer, and a piece of $\frac{1}{4}$ inch pipe 6 inches long. Put them together as shown in the cut.

FIG. 22.

and placed in ovens somewhat the shape of a beehive, a limited supply of air is admitted on top of the slack, the heat of the oven ignites it, and the combustion is continued as long as smoke is evolved. When this ceases, the air supply is cut off and the oven allowed to cool for about twelve hours; the coke is then quenched with water. Coke thus prepared is superior to all other fuels for iron smelting; while it does not burn as rapidly as charcoal, and therefore does not produce quite as high a temperature, it is able to resist the pressure caused by the weight of ore and flux in the highest furnaces. Charcoal can only be used in the smaller furnaces, because it is crushed by the great weight above it. Anthracite, on the other hand, is able to withstand the mechanical effects, but it burns so slowly that it does not produce the required temperature. Coke, therefore, combines the good qualities of both charcoal and anthracite; it yields the required temperature and is able to withstand the charge in the highest furnaces.

For domestic purposes, coke is an economical fuel, and possesses the further advantage of being smokeless, but is under the disadvantage that when the temperature of the combustion falls off to any considerable extent, the carbon dioxid produced may be delivered into the living rooms instead of being carried off by the chimney.

308. Coal. — Examination of the various varieties of coal shows that they represent various stages in the natural destructive distillation of vegetable refuse. When a mass of such refuse is covered with a layer of clay or mud so as to exclude the air, and is subjected to pressure due to the accumulation of rock above it, or to heat from beneath it, a complex molecule of cellulose, $C_{36}H_{60}O_{30}$ (woody fibre), is broken up just as it is in a retort, the composition of the

residue depending upon the degree of heat and the amount of pressure to which the deposit has been subjected. According to one theory, petroleum and natural gas are the liquid and gaseous products of the distillation. The objection to this theory is that the occurrence of petroleum seems to have no necessary connection with the occurrence below of coal seams. The most probable theory seems to be that both petroleum and coal are formed from organic matter, but of different conditions, and that natural gas is derived chiefly from the slow distillation of petroleum. That each of these substances has been formed by the destruction of organic matter may be regarded as certain. These processes have been in progress through long geological eras, and the coal of the older formations is more completely transformed than that of the recent formations. *Anthracite* or *hard coal* corresponds to the coke left in the gas retort, and is nearly pure carbon. It occurs only in the older geological formations, and in these formations only in locations showing that the region has been upturned, thus subjecting the coal to high temperature and great pressure. Anthracite burns without flame or smoke, and ignites with difficulty.

Bituminous or *soft coal* also occurs in the older geological formation, but the evidences of high temperature and great pressure are always lacking; it is softer than anthracite, and burns with a smoky flame. *Lignite,* or *brown coal,* occurs in more recent geological formation, and often retains the structure of the wood from which it was formed.

Peat is an open mass of vegetable refuse of recent formation. The following table, showing the compositions of these substances, will give the student an idea of the nature of the changes which the various kinds of coal have undergone: —

	C	H	O
Wood	49.7 %	6.2 %	43 %
Peat	59.5	5.5	33
Brown Coal	68.7	5.5	25
Bituminous Coal	81.2	5.5	12.5
Anthracite Coal	95	2.5	2.5

309. Ammonia from Compost Heaps. — When marsh gas is formed in nature it is a product of decay; the molecules of the decomposing substance breaking up into simpler molecules. Animal substances usually contain carbon, hydrogen, nitrogen, and oxygen. When they decay in a limited supply of air, the oxygen combines with the carbon and hydrogen, and if there is not enough to oxidize all of these elements, some of the carbon is given off, combined with hydrogen, as marsh gas. The nitrogen also combines with hydrogen as ammonia gas (NH_3). These two substances may be regarded as intermediate products in the process of decay. Some animal substances give off ammonia when they decompose in air, but many others yield it when the process is carried on in a limited supply of air.

REVIEW QUESTIONS

1. Describe the process of destructive distillation as employed on an extensive scale in the industrial arts. State reasons for employing this process.

2. Describe the preparation of coke, and state for what and why it is used.

3. Discuss petroleum as to (*a*) origin, (*b*) method by which obtained, (*c*) products.

4. State the theory of the formation of (*a*) coal, (*b*) petroleum, (*c*) natural gas.

5. Describe the process of destructive distillation as accomplished by nature on an extensive scale.

6. Account for the formation of ammonia in compost heaps.

7. Should destructive distillation be considered a process of oxidation or of reduction ?

CHAPTER XXIX

FERMENTATION

310. Definition. — As suggested by its derivation, from "*fervere*" (to boil), this term was originally applied to all chemical changes involving the effervescence of a liquid. In its modern acceptance, however, it has nothing at all to do with effervescence, being used to designate a peculiar class of decompositions which is produced in complex organic substances by certain living organisms, or by chemical compounds formed by these organisms. The most familiar illustrations of fermentation are the fermentation of fruit juices, or fruits, the souring of cider, the decay of vegetable matter, the putrefaction of nitrogenous matter, the souring of milk, and that which occurs in the process of making bread.

Fermentation occurs more rapidly in the presence of moisture than in dry substances, and the process is more active at temperatures between 25° and 35° C. than at either higher or lower temperatures.

Most organic substances are subject to fermentation, although those of simple molecular structure are less subject to it than the complex molecules, and a few of these like cresol, phenol, or creosote are valuable agents for the prevention of fermentation. The chemical changes consist in the breaking down of complex molecules, forming simpler groups of atoms, either by the absorption of the hydrogen and oxygen of water, or by slow oxidation; but in some

cases it consists in a rearrangement of the atoms in the molecule, forming an isomeric compound.

The changes cannot be induced by any means except the presence of ferments, and each ferment produces its special change, which is often the precise opposite of that which the chemical properties of the elements forming the molecule which is decomposed would lead us to expect.

311. Ferments. — Most ferments are microscopic plants of very simple structure, which multiply with great rapidity; they derive the material needed for their growth from the medium in which they are placed, transforming it into other substances. They are variously known as germs, microbes, bacteria, etc.

Yeast, the most familiar of these ferments, is a microscopic plant found in the air and about certain fruit trees. The yeast of the store is grown on some suitable culture medium, as the potato or corn meal.

Besides these organized ferments which cause fermentation as a result of their peculiar life processes, there is a group of chemical, or unorganized ferments, known as *enzymes*, of which diastase, pepsin, and ptyalin are examples. Although the enzymes are not living organisms, they are all derived directly from animal or vegetable life. The chemical action caused by the enzymes is not well understood; the decompositions are less complete than those due to organized ferments, and usually consist simply of a rearrangement of the atoms of the molecule. Like organized ferments they are most active at certain temperatures, which vary for the different ferments. Their characteristic properties are destroyed when their aqueous solution is heated to the boiling point, but in a dry state they can withstand a much higher temperature; pepsin, for example,

may be heated to 170° C. without losing its ability to cause fermentation. There is some doubt as to whether the real cause of fermentation is the microscopic organism, to which the action is usually attributed, or a chemical compound excreted by the organism.

312. Alcoholic Fermentation. — The fermentation induced by yeast converts sweet fruit juices and solutions containing a sugar known as glucose, $C_6H_{12}O_6$, into ethyl alcohol, C_2H_6O; carbon dioxid is liberated, and one or two other substances are formed, but the principal reaction is: —

$$C_6H_{12}O_6 = 2\,C_2H_6O + 2\,CO_2.$$

Several microörganisms besides yeast induce alcoholic fermentation, and they are so abundant that all fruit juices seem to ferment spontaneously; the ferment, however, is either obtained from the air or was clinging to the outside of the fruit. The fermented liquors which are obtained vary as widely in their properties as do the fruits from which they are made, and are known by different names. Hard cider is fermented apple juice, wine is fermented grape juice, perry is fermented pear juice.

The percentage of alcohol in wine varies considerably; if the fermentation is checked before all of the sugar has been converted into alcohol, a sweet wine is obtained which will contain less alcohol than it would have contained if the fermentation had been allowed to proceed; besides this, the amount of sugar which may be converted into alcohol is greater in some grapes than in others. Perhaps the average amount of alcohol in wine is between 15 and 20 %.

Alcoholic fermentation occurs only in a dilute solution of some sugar, but certain of the several ferments which induce it can convert other substances into a sugar; for this reason alcoholic fermentation often occurs in substances containing starch, but it is always preceded by a reaction

which converts the starch into sugar. In the process of brewing ale and beer the first step is to convert the barley into malt; the maltose, a sugar found in the malt, is then extracted, to this yeast is added, and the fermentation which ensues yields a liquid containing between 3 and 9 % of alcohol. In the manufacture of whiskey, the Indian corn, rye, or other grain undergoes a similar change before alcoholic fermentation takes place. This is also true of the flour in the process of bread making.

Experiment CXX. A Study of Alcoholic Fermentation. — 1. Dissolve about a teaspoonful of glucose in 100 cc. of water in a flask, add a small piece of yeast, and arrange a delivery tube so that any gas which may be evolved shall bubble through lime-water.

2. Set the apparatus in a warm place for twenty-four hours.

3. Examine the lime-water for evidence that carbon dioxid has been evolved.

4. Arrange a test tube in a bottle of cold water in such manner that it may serve as a condenser, heat the flask very gradually, receiving the vapor in the test tube.

5. Examine the first few drops condensed, noting odor, combustibility, etc.

313. Bread Making.

Alcoholic fermentation plays an important part in making bread, but the changes which occur in the oven are not less interesting. Taken together these two processes convert the comparatively indigestible flour into one of our most wholesome foods. It is worth our while to consider briefly the various steps in the process, with the objects to be attained in each.

(*a*) *The Mixing.*

Flour, salt, yeast, and milk or water are mixed into dough. In this process the starch granules are to be thoroughly moistened, and the yeast evenly distributed through the mass. The latter object may be best accom-

plished by vigorously beating with a spoon, when enough of the flour has been added to give the mixture the consistency of a rather thick batter; much oxygen from the air is at the same time distributed through the mass. After ten or fifteen minutes' beating the remainder of the flour is worked in, and the dough set in a warm place (75° F.) to rise. It is desirable that all of the flour required be added at this time, as the flour is rendered more digestible, and acquires a better flavor from fermentation.

The addition of a little sugar renders the fermentation more rapid. The use of milk instead of a part of the water is strongly recommended, as it materially increases the value of the bread as a food.

(*b*) *The Fermentation.*

In this process, which lasts about three hours under proper conditions, some of the starch is changed to sugar, and then to alcohol and carbon dioxid; the gluten is modified and perhaps combined with the starch granules, and the albumen is rendered insoluble. The escape of the gases is hindered by the hydrated gluten, which is elastic, and as the gases form, the mass increases in bulk and becomes porous. If the fermentation continues too long, acetic fermentation sets in, and the mass becomes sour.

(*c*) *The Baking.*

As the temperature of the dough rises, the starch granules burst, the yeast is killed and fermentation ceases, the gases are expanded, increasing the porosity of the dough, some of the water together with a portion of the carbon dioxid and of the alcohol are expelled, the albumen is coagulated and rendered more digestible, some of the starch is changed into dextrin, some caramel is formed in the crust, and a distinct flavor is developed.

314. The Formation of Acids by Fermentation. — In all alcoholic fermentation, including the fermentations which form other kinds of alcohol than that produced by yeast, the molecule of the substance acted upon takes hydrogen and oxygen, and all of the alcohols formed have basic properties. We now consider a kind of fermentation which yields an acid product. Familiar examples of this kind of fermentation are the souring of milk and the souring of cider or wine.

315. Acetous Fermentation. — This kind of fermentation is due to the action of a ferment commonly known as vinegar plant, or as "mother of vinegar." It is a micro-organism, and in no way related to the so-called vinegar eels which are sometimes seen in vinegar. The acetous ferment attacks alcoholic liquids, and changes the alcohol which they contain into acetic acid, with the following reaction: —

$$C_2H_6O + 2\,O = C_2H_4O_2 + H_2O.$$

It should be noted that this is a process of oxidation.

If acetic fermentation is not checked, the acetic acid formed is oxidized to carbon dioxid and water.

316. Vinegar is a liquid containing from 2 to 4 % of acetic acid. It is ordinarily prepared by introducing the acetous ferment into cider, wine, or other liquid containing a small per cent of alcohol. The process proceeds very slowly. The so-called mother of vinegar, which is commonly used to start acetous fermentation in a fresh cask of the liquid to be fermented, is a mass of minute plants which is found in most samples of vinegar.

317. Putrefaction and Decay. — The term *putrefaction* is employed to denote a process of fermentation developed in

nitrogenous organic substances by microörganisms, which is accompanied by the evolution of foul odors.

This action is entirely distinct from the decomposition due to the action of oxygen, although under ordinary conditions these two processes occur simultaneously.

The decay of wood and other vegetable tissue, and the destruction of textile fabrics by mildew, are due to the action of microörganisms, which require both oxygen and moisture in their life processes; for this reason these varieties of fermentation do not occur in perfectly dry substances, nor in those which are immersed in water.

318. Methods of Preventing Fermentation. — Various methods of preventing the decay of organic matter used for food are in common use. In all of them the growth of the ferment organisms is prevented, either by bringing about conditions unfavorable to such growth, or by the use of chemical agents which destroy or retard the growth of the organisms. The following methods may be mentioned by way of illustration: —

1. *Drying.* — Ferments cannot grow without water; hence dried fruit, dried meats, and condensed milk keep much longer than when in their normal condition.

2. *Cold Storage.* — The efficiency of cold storage depends upon the fact that most ferments are inactive at low temperatures.

3. *Canning.* — In the process of canning meats, fruits, and vegetables, the material is raised to a high temperature (not necessarily to the boiling point), to destroy all ferments, and the cans are sealed while the material is still hot.

4. *By the Use of Alcohol or Vinegar.* — In certain kinds of fermentation the action diminishes in vigor as the product of the chemical action increases, and finally ceases when a

definite percentage of the product has accumulated. It thus appears that the product of the fermentation has an inhibitory effect upon the chemical action, if, indeed, it is not poisonous to the ferment organism. This is the case in both alcoholic and acetous fermentation; hence the use of alcohol as a preservative agent in brandied fruits, and vinegar in pickles.

5. *Preserving and Spicing.* — Spices and heavy syrups prevent the growth of ferments, and fruits are often preserved, even when exposed to the air, by covering them with syrups or strong infusions of spices.

6. *By the Use of Antiseptics.* — Among the chemical agents employed as antiseptics are: common salt, used in curing meats and fish; and wood smoke, which is used to preserve hams, tongue, fish, etc., because of the creosote which it contains. Salicylic and boracic acids have also been used to some extent in preserving meat and fruits, but the propriety of such use is at least questionable, as it is a well-known fact that even in comparatively small doses they interfere with digestion.

The decay of wood is materially lessened by impregnating it with some antiseptic, such as carbolic acid or creosote, and mildew in canvas is prevented by saturating the fibres of the cloth with zinc carbonate, lead sulfate, or some similar substance.

REVIEW QUESTIONS

1. What is yeast? For what is it used? Explain the chemical action involved in this use.

2. Define fermentation. What substances are subject to fermentation? What is the general character of the chemical changes produced?

3. Describe the process of making bread. What is the object of the fermentation? What chemical changes occur in the oven?

4. Discuss the acetous fermentation. What is vinegar? How is it prepared?

5. Why does milk sour?

6. Mention eight ways in which the decay of fruits may be prevented.

7. In what four ways may meats be preserved?

8. Mention five processes based upon alcoholic fermentation.

CHAPTER XXX

PHOSPHORUS

Symbol P. — Atomic Weight 31

319. Occurrence. — In combination with oxygen and metals, phosphorus is widely distributed in nature. Calcium phosphate is present in all fertile soils, and has been shown to be necessary to the growth of plants; it forms about 60 % of the bones of animals. In the mineral kingdom several phosphates occur.

320. Preparation. — Phosphorus is prepared by treating calcined bones with sulfuric acid. The following reaction occurs: —

$$Ca_3(PO_4)_2 + 3\,H_2SO_4 = 3\,CaSO_4 + 2\,H_3PO_4.$$

The calcium sulfate is insoluble in water, and is separated from the solution of orthophosphoric acid by filtration; the solution is concentrated, mixed with carbon, and distilled in bottle-shaped clay retorts. When the retort reaches a white heat, the phosphorus distills over, and is condensed under water. The crude phosphorus thus obtained is refined by processes which are carefully guarded as trade secrets.

321. Physical Properties. — When freshly prepared, phosphorus is a colorless, transparent, wax-like solid which gradually becomes coated with a film which is at first white, then yellow, brown, red, and finally black. At

0° C. it is brittle, but at ordinary temperatures it is flexible; it melts at 44°, and boils at 290°. It is insoluble in water, but dissolves readily in carbon disulfid, and less freely in chloroform, alcohol, petroleum, and other solvents. When a solution of phosphorus in carbon disulfid is evaporated, the phosphorus is left in exceedingly minute particles, and if the evaporation takes place on a non-conductor of heat, the oxidation will raise the phosphorus to its kindling temperature, and cause it to burst into flame.

Experiment CXXI. — 1. Pour 2 or 3 cc. of a solution of phosphorus in carbon disulfid on a piece of filter paper.

2. Place the paper on the base of your retort stand, and observe any changes that occur. Do you note the formation of crystals of phosphorus? Are white fumes evolved?

3. After the burning has ceased, examine the paper. Is it entirely consumed? Do you discover a coating on portions of the paper which might have prevented its burning? On which portions is it thickest? From what source might such a coating have been derived?

322. Chemical Properties. — Phosphorus belongs to the nitrogen family, but its chemical activity is in sharp contrast with that of nitrogen. It is one of the most active elements.

When exposed to the air phosphorus is slowly oxidized and gives off fumes which are faintly luminous and visible in a dark room; if its temperature is slightly increased, as by the heat of the hand or by friction, it bursts into flame; for this reason phosphorus is always kept under water, and should also be cut only under water. Its kindling temperature is 60°, and its specific gravity 1.82.

The name *phosphorus* is derived from the Greek, and means *light bearing*. The mark left by a match on any surface in a dark room is phosphorescent. The affinities of phosphorus for oxygen and for iodin have been illus-

trated. It has also strong affinity for sulfur and for the halogens, and it combines directly with the metals, forming phosphids.

Phosphorus is a powerful poison; in large doses it causes death in a short time, and in smaller doses produces intense pains in the stomach, and usually brings on convulsions.

323. Red Phosphorus. — This important allotropic modification of phosphorus may be formed by subjecting the ordinary variety to the action of light, heat, or electricity. In the arts it is prepared by heating ordinary phosphorus in cast iron retorts, from which air is excluded, to between 240° and 250° C., by means of a bath of melted solder. If the temperature rises to 300°, the red phosphorus is changed back to the ordinary variety. After fifty or sixty hours of heating at 240°, there is found in the retort a layer of hard lumps of red phosphorus containing a small percentage of the ordinary variety. To remove this, the material is ground to a powder under water, and treated with a solution of caustic soda, or with carbon disulfid, either of which dissolves the ordinary phosphorus.

If one part of iodin be added to 100 parts of the ordinary or vitreous phosphorus, and the mixture is heated, the change to red phosphorus occurs below 200° C.

324. Properties of Red Phosphorus. — Red phosphorus is a chocolate-red, amorphous powder; it is odorless, opaque, and insoluble in the solvents of the ordinary variety; it is not poisonous.

In dry air, at ordinary temperatures, there is practically no oxidation, and therefore no phosphorescence, but in the presence of moisture it is very slowly oxidized.

The melting point of red phosphorus is evidently above the temperature at which it changes back to the ordinary

variety, for it has never been melted. It is somewhat heavier than ordinary phosphorus; specific gravity, 2.25. Active combustion begins in air at 300°, the product of the combustion being identical with that of the ordinary variety.

325. Uses of Phosphorus. — The principal use of phosphorus is in the manufacture of matches, although small amounts are used annually in poisons for rats and vermin. Its compounds, the phosphates, are used as fertilizers, and certain other compounds are used in medicine and in the laboratory.

Matches. — The process of manufacturing the common sulfur match was described in § 161; the disagreeable odor of such matches is obviated if paraffin or stearin is used instead of sulfur, and matches prepared in this way are often called "parlor matches." The following is one of the many recipes for a paste with which to tip parlor matches: —

Vitreous phosphorus	6.4 parts
Lead dioxid	50 "
Dextrin	30.6 "
Water	13 "
	100 "

Most parlor matches made in this country contain potassium chlorate instead of lead dioxid as the oxidizing agent; such matches snap and burn with great vigor, but the heads sometimes fly off, inflicting severe burns or causing fires.

Various attempts have been made since the discovery of red phosphorus to prepare a non-poisonous match; the efforts were comparative failures except the *safety match.* These matches do not contain phosphorus, but some makers put other poisons in the paste. The Swedish safety matches

are tipped with a paste made of antimony sulfid, potassium chlorate, and glue; they are ignited by rubbing them upon the side of the box, which is coated with a paste made of red phosphorus, antimony sulfid, and glue. In several European countries the use of any other kind of match is prohibited by law.

The paste with which all matches are tipped consists of one or more oxidizable substances mixed with compounds which can supply oxygen.

In the common match one of the oxidizable substances is phosphorus, which requires but little friction to ignite it. When the oxidizing agent is potassium chlorate, the phosphorus is oxidized, and potassium chlorid remains.

In the safety match, the match head contains antimony sulfid as the oxidizable substance and an oxidizing agent, while the rubbing surface contains no oxidizing agent; this lack of oxygen prevents the combustion of the rubbing surface when the match is struck.

The only difference between the chemical actions in the heads of the common and the safety match is, that in the former, phosphorus is oxidized, and in the latter, antimony sulfid is oxidized.

326. Oxids of Phosphorus. — Like nitrogen, phosphorus forms several compounds with oxygen; the best known of them are the trioxid, P_4O_6, and the pentoxid, P_2O_5.

327. Phosphorus Trioxid, P_4O_6, is a white crystalline solid formed by the slow combustion of phosphorus in a limited supply of air. It is slowly dissolved by cold water, forming phosphorous acid, H_3PO_3. In hot water violent action occurs in which the spontaneously inflammable hydrogen phosphid, PH_3, is evolved and red phosphorus is formed.

328. Phosphorus Pentoxid, P_2O_5, is a snow-white amorphous, odorless, very voluminous powder. It is the chief product formed when phosphorus burns in air or in oxygen, and was formed in Experiments 30, 56, and 57. It is very deliquescent, dissolving in the water absorbed if exposed to

moist air for a short time, it must therefore be kept in glass tubes closed at both ends. When thrown into water it dissolves with a hiss, forming metaphosphoric acid. Its affinity for water is its most important property and makes it our most useful desiccating agent. The same property enables it to decompose nitric acid as follows: —

$$2\,HNO_3 - H_2O = N_2O_5,$$

and to abstract water from many compounds containing carbon, hydrogen, and oxygen, thus converting them into hydrocarbons.

329. The Phosphorus Oxyacids. — Phosphorus combines with hydrogen and oxygen to form several acids. Three of the more common are

Hypophosphorous acid,	H_3PO_2
Phosphorous acid,	H_3PO_3
Phosphoric acid,	H_3PO_4

Hypophosphorous acid is monobasic and is chiefly important because of the value of its salts in medicine.

Phosphorous acid is dibasic and is of little importance save from a theoretical standpoint.

Phosphoric acid is the most important of the acids; its salts are the principal compounds of phosphorus.

Phosphorus pentoxid combines with water to form three distinct acids: *Metaphosphoric Acid, HPO_3,* formed when the pentoxid dissolves in cold water —

$$P_2O_5 + H_2O = 2\,HPO_3;$$

Orthophosphoric Acid, H_3PO_4, formed when the pentoxid dissolves in boiling water, —

$$P_2O_5 + 3\,H_2O = 2\,H_3PO_4;$$

and *Pyrophosphoric Acid*, $H_4P_2O_7$, which is not formed by direct combination.

Orthophosphoric acid may be converted into either of the others by the application of heat. At 213° it is converted into pyrophosphoric acid with the following reaction: —

$$2\,H_3PO_4 = H_4P_2O_7 + H_2O.$$

At 400° metaphosphoric acid is formed.

$$H_4P_2O_7 = 2\,HPO_3 + H_2O.$$

Metaphosphoric acid is monobasic, orthophosphoric acid is tribasic, and pyrophosphoric acid is tetrabasic; from these three acids, therefore, eight different salts, phosphates of a univalent metal, may be formed.

330. Phosphoric Acid, H_3PO_4, or orthophosphoric acid, as it is sometimes called, may be prepared in several ways besides that described in the last article; as, for example, by oxidizing phosphorus with nitric acid, or by decomposing bone-ash, $Ca_3(PO_4)_2$, with sulfuric acid, as in the preparation of phosphorus. The solution thus obtained is evaporated to a thick syrup, from which hard, colorless, prismatic crystals, which are very deliquescent, may be obtained.

As phosphoric acid is tribasic, it forms three series of salts; thus the metal sodium forms the following phosphates: —

Trisodium phosphate,	Na_3PO_4
Hydrogen disodium phosphate,	HNa_2PO_4
Dihydrogen sodium phosphate,	H_2NaPO_4

The first of these is the normal phosphate, and the others are called acid phosphates. We have here, as we had in the case of the acid sodium carbonate, an acid salt which

gives an alkaline reaction with litmus paper. For this reason there is some objection to the classification of salts as acid and normal, and the suggestion that they be called primary, secondary, tertiary, etc., depending upon the number of atoms of a metal which the molecule contains, has been somewhat favorably received. The common sodium phosphate is the second of the three mentioned above.

There are several important double phosphates formed by replacing part of the hydrogen of the acid with one metal and the rest with another, ammonium magnesium phosphate, NH_4MgPO_4; and hydrogen sodium ammonium phosphate, $HNaNH_4PO_4$, commonly called *microcosmic salt*, are examples of the double salts.

331. Allotropism. — Phosphorus presents one of the best illustrations of allotropism, not only because of the difference in the physical and chemical properties of the varieties, but also because of the ease with which either variety may be converted into the other. In addition to the two modifications of phosphorus already described, a metallic form is known, but it is rare and of little use.

Allotropism is similar to polymerism, defined in § 337, but the term is usually applied to elements instead of compounds. Some writers, however, apply the term to those compounds existing in two forms, which differ only in their physical properties.

It is probable that as our knowledge increases we shall be able to prove that all cases of allotropism are due to differences in the number of atoms in the molecule of the element. In the case of ozone, which is an allotropic modification of oxygen, this has already been proven by the change in volume and in vapor density, which occurs when oxygen is transformed into ozone, or when the reverse

change takes place. A molecule of oxygen consists of 2 atoms, and its vapor density is 16, whereas the molecule of ozone consists of 3 atoms, and its vapor density is 24.

332. Ozone. — Oxygen is best converted into ozone by subjecting it to the silent discharge of an induction coil. It is also converted into ozone by the electrolysis of dilute sulfuric acid, and by the slow oxidation of phosphorus.

Prepared by either of these methods the ozone is very dilute, rarely forming more than one-fifth of the whole. Ozone has a strong odor, somewhat resembling that of chlorin; it irritates mucous membranes, and quickly induces headache. At $-106°$ it condenses to a dark blue liquid; it is more energetic chemically than oxygen, quickly bleaching, disinfecting, and even destroying organic substances by oxidation. Many metals not affected in oxygen are attacked by ozone. Ozone is sometimes considered as oxygen oxid, O_2O. It often acts as a reducing agent, taking oxygen from other substances and changing to the ordinary form of oxygen,

$$O_3 + O = 2\,O_2.$$

This is believed to be its action on the blood. Ozone is produced in air by lightning discharges, and is usually present in country air. Its characteristic odor proves its presence also in the air near a static electric machine.

REVIEW QUESTIONS

1. Describe the preparation of phosphorus. State the properties and two important uses of phosphorus.
2. Describe an experiment illustrating the affinity of phosphorus for iodin.
3. Explain the difference between the chemical action of the ordinary friction match and that of the safety match, stating the substances from which each is made.

4. Describe a method of preparing phosphoric acid. Give the names, formulas, and methods of preparation of two acids formed from phosphoric acid.

5. Give the name and properties of the substance formed by the union of phosphorus pentoxid and hot water, and write the reaction.

6. Discuss allotropism. Illustrate by phosphorus and carbon.

7. Contrast the characteristics of two forms of phosphorus.

8. Mention two forms of oxygen. State the difference between them, and state a theory to account for the difference in their effects.

9. Give the name and formula of a monobasic acid, of a dibasic acid, of a tribasic acid. Give the names and formulas of salts formed by the acids named.

10. Define tribasic acid, and give an example with formula. Classify as normal or acid three salts formed from this acid, and give the formula of each.

11. Write the name and formula of a normal salt, an acid salt, a double salt. Show how these three classes of salts are related to one another.

12. Describe the chemical changes which occur when phosphorus is burned in oxygen and the product dissolved in water.

13. State an objection to the use of the term *acid salt*.

14. In what respects are the properties of ozone similar to those of chlorin?

CHAPTER XXXI

ARSENIC

SYMBOL As. — ATOMIC WEIGHT 75

333. Occurrence. — Arsenic is found free in nature, but occurs much more abundantly in combination with other elements. Its principal ores are arsenolite, As_2O_3; realgar, As_2S_2, the red sulfid; orpiment, As_2S_3, the yellow sulfid; arsenopyrite (mispickel), FeSAs; and arsenical iron, $FeAs_2$.

334. Preparation. — Arsenic is obtained as a by-product in the process of reducing certain ores, but most of the arsenic of commerce is obtained from arsenopyrite. The ore is heated in covered iron pots, out of contact with the air, when the arsenic vaporizes without visible liquefaction and condenses as a steel-gray powder on the cooler portions of the apparatus.

335. Properties. — Arsenic is a very brittle steel-gray substance, having a metallic lustre; it is a good conductor of heat and electricity. At ordinary pressures it cannot be melted, but passes directly into the aeriform state. If heated in a sealed tube under great pressure, however, it may be liquefied. At low temperatures its vapor density shows that, like phosphorus, it is tetratomic, but at high temperature it is diatomic; it exists in at least two allotropic forms, a crystal and an amorphous substance, either of which is readily transformed into the other. It burns in oxygen with a bluish flame. It will be observed that its

physical properties resemble those of a metal, and in some of its chemical properties it is like a metal; for example, it combines with the members of the chlorin family and forms alloys with the metals; its oxids, however, are acid-forming, and in several other chemical properties it resembles the acid-forming elements. It is one of the elements which lie between the metallic and the non-metallic elements which are known as metalloids. The addition of a small amount of arsenic to a metal increases its fluidity in the liquid state and increases its hardness when in the solid state; it is therefore added to lead which is to be made into shot.

336. Compounds of Arsenic and Oxygen. — Two compounds of arsenic and oxygen are known, arsenious oxid, As_4O_6, and arsenic oxid, As_2O_5. The formula of the first was formerly written As_2O_3, and it was known as the trioxid, but it has been proven that its vapor density is 198, which corresponds with the formula As_4O_6. Arsenic oxid is unimportant, and will not be discussed.

337. Arsenious Oxid, As_4O_6. — This is the principal compound of arsenic known in commerce; it is commonly known as arsenic, or more rarely as white arsenic or as arsenious acid.

As has been stated, this substance occurs in nature. It may be prepared by heating metallic arsenic or an arsenical ore in a stream of oxygen or air and condensing the vapors. Arsenious oxid occurs in three forms: —

1. An amorphous, vitreous mass, somewhat more soluble in water than the other varieties, which gradually changes to the second form.

2. An octohedral crystal, which is converted into the amorphous modification by fusion.

3. A prismatic crystal.

The amorphous modification dissolves sparingly in water, requiring 108 parts; its solubility is somewhat increased by acidulating the water with hydrochloric acid.

Arsenious oxid is a violent poison; a dose of two decigrammes usually proves fatal, but men employed in arsenic works and habitual users of arsenic often take much larger doses without apparent injury. The fact that arsenious oxid has neither taste nor smell accounts for its use in so large a proportion of the cases of criminal poisoning.

The water solution of arsenious oxid has a feeble acid reaction, which is probably due to the presence of a small quantity of arsenious acid, but the acid has never been isolated. Three classes of salts of this unknown acid are readily obtained; they are known as ortho-arsenites, meta-arsenites, and pyro-arsenites, and correspond to the three classes of salts formed by phosphoric acid.

Arsenious oxid is used in making certain pigments, as Scheele's green, $CuHAsO_3$, and Schweinfurt green, a compound of the arsenite and acetate of copper commonly called Paris green. It is also used as an oxidizing agent in glass making; in very small doses it is used in medicine, and small quantities are consumed each year in the preparation of vermin poisons.

Compounds which, like arsenious oxid, exist in two or more forms which are identical in percentage composition and molecular weight, but which differ in physical or chemical composition or both, are said to be *isomeric* and the phenomenon is known as *isomerism*.

Compounds which are identical in percentage composition but which differ in molecular weight and properties are said to be *polymeric* and the phenomenon is known as *polymerism*. Acetylene, C_2H_2, and benzene, C_6H_6, are polymeric.

338. Hydrogen Arsenid, AsH_3 (Arsin). — Like nitrogen, phosphorus and arsenic each furnish a gaseous compound

containing three atoms of hydrogen. The arsenic compound is important because it gives us one of our more valuable tests for arsenic.

Hydrogen arsenid is formed when a soluble arsenic compound is acted upon by nascent hydrogen. It is a colorless gas with a strong, repulsive odor, extremely poisonous even when very dilute, more than one chemist having lost his life through the accidental inhalation of the gas. It may be liquefied at $-40°$, it burns with a bluish white flame, evolving fumes of arsenious oxid. If the gas be passed through a solution of silver nitrate, metallic silver is precipitated and the arsenic is found in the solution.

Experiment CXXII. Marsh's test for arsenic. — 1. Fit a small flask with a two-holed stopper, *c*, carrying a safety tube in one hole and a delivery tube drawn out to a point in the other.

2. Put a few pieces of zinc in the flask, cover them with water, and add dilute hydrochloric acid until brisk effervescence occurs.

3. Holding the flask in the hand, collect the evolved hydrogen over water in a test bottle. Test each bottle of the gas obtained.

4. When the air is expelled from the apparatus and the gas burns quietly, pour a few drops of a solution of arsenious oxid through the safety tube, ignite the gas and hold a concave piece of porcelain, as a piece of an evaporating dish, in the flame. Keep the gas alight. Describe the deposit formed on the porcelain.

Soluble compounds of antimony form a similar deposit which has no lustre and is blacker; but the antimony spot dissolves in ammonium sulfid, whereas that of arsenic does not dissolve unless heated. There is no substance which can be identified by the chemist more positively than arsenic. The Marsh test will detect the slightest trace of the poison.

339. Complete and Incomplete Combustion. — The principles developed in § 272, p. 170, explain the formation of

the arsenic "mirror." When arsin burns normally, the following reaction occurs: —

$$4\ AsH_3 + 6\ O_2 = As_4O_6 + 6\ H_2O.$$

When a cold object is held in the flame, thus excluding the air and lowering the temperature of the flame below the kindling temperature of arsenic, the following reaction occurs: —

$$4\ AsH_3 + 3\ O_2 = As_4 + 6\ H_2O.$$

There are many cases similar to the above; the preparation of lampblack, § 270, is one of them. When marsh gas burns in air the following reaction occurs: —

$$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O.$$

In a limited supply of air the reaction is approximately as follows: —

$$CH_4 + O_2 = C + 2\ H_2O.$$

Similarly, the perfect combustion of hydrogen sulfid and carbon disulfid are expressed by the following equations: —

$$H_2S + 3\ O = H_2O + SO_2,$$

$$CS_2 + 3\ O_2 = CO_2 + 2\ SO_2,$$

and the incomplete combustion by the following: —

$$H_2S + O = H_2O + S,$$

$$CS_2 + O_2 = CO_2 + 2\ S.$$

REVIEW QUESTIONS.

1. In what compound is the element arsenic found in nature? What are its properties?

2. What compound does arsenic form with hydrogen? To what compound of nitrogen is it analogous? How is it formed?

3. What is the substance which is usually called arsenic? How is it obtained from the element arsenic, and from the compounds of arsenic with metals? What are its properties?

4. State the properties and uses of arsenic, and describe a process for obtaining it.

5. Describe the characteristics and process of manufacture of arsenious oxid.

6. Explain why so many substances unite with the sulfur of hydrogen sulfid more readily than they do with free sulfur.

7. Describe Marsh's test for arsenic.

8. Compare the formation of the metallic mirror, of Marsh's test for arsenic, with the deposition of soot on a cold body held in a candle flame.

9. Compare the products of the complete combustion of hydrogen arsenid with the products formed when the combustion is rendered incomplete by holding a cold porcelain dish in the flame, writing the reactions in both cases.

CHAPTER XXXII

QUALITATIVE ANALYSIS

340. Apparatus. — For this work the following additional apparatus will be required: —

6 test tubes	2 small breakers
1 evaporating dish	1 wash bottle
filter paper	1 test-tube stand
2 funnels	1 pair forceps
1 sand bath	litmus paper

8 reagent bottles, 150 or 200 cc.

(Keep litmus paper in small box or bottle.)

341. Reagents. — The solutions used in analysis should be prepared by each student from chemically pure substances dissolved in distilled water. See that the bottles are clean.

Experiment CXXIII. — Prepare 150 cc. of each of the following reagents: —

Hydrochloric acid, 1 part acid to 4 parts water.
Nitric acid, 1 part acid to 4 parts water.
Ammonium hydroxid, 1 part 26° ammonia water to 3 parts water.
Ammonium sulfid, the above saturated with hydrogen sulfid.
Ammonium carbonate, 1 part to 4 of water + 1 part ammonium hydroxid.
Ammonium chlorid, 1 part to 8 of water.
Sodium hydroxid, 1 part to 8 of water.
Sulfuric acid, concentrated.

342. Suggestions. — 1. Keep all apparatus clean; rinse it with water, using brush when necessary. If not cleaned with water, try concentrated nitric or nitrohydrochloric acid. Never use brush with

acids. Tubes may be cleaned in one-fourth the time if not allowed to stand till dry.

2. Hold test tubes in fingers when heating them; keep the tubes moving.

3. Never lay the stoppers of reagent bottles down. Hold them between the little finger and the palm and replace them promptly; this avoids mixing reagents.

4. When applying reagents, hold the tubes on a level with the eye and add the reagent, a drop at a time.

5. You will have enough to do without attending to the work of your neighbor.

6. You are responsible for the good order of your locker, drawer, and table. The table must be left clean and dry at the close of each period.

7. All solid matter to be thrown away must be deposited in jars. If thrown in the sink the waste pipe will become clogged.

8. Never carry reagent bottles from the side table to your table but use them at the side table and replace them.

343. Precipitates. — A precipitate is a substance which falls to the bottom of the vessel containing a solution, on the addition of some other substance capable of producing a chemical change. Chemical changes may occur when solutions are mixed, without forming precipitate, if all of the products of the reaction are soluble in the liquid. When a precipitate is formed, however, it is always evidence of chemical change, and when one of the products is a solid, it may be separated from the substances in solution by filtration. For this reason one of the systems of qualitative analysis is based upon the formation of precipitates when the substance to be analyzed is treated with certain reagents.

344. Grouping of the Metals. — In order to determine which of the common metals forms precipitates when treated with various reagents, test four or five cubic centimetres by adding the reagent drop by drop. If the sub-

stance is not in solution, it will be necessary to dissolve it before beginning the analysis.

Experiment CXXIV. — 1. Determine which of the following metals are precipitated by hydrochloric acid.

2. Record the color of the precipitate and write the reaction.

3. Test at least one salt of each of the following metals: —

Aluminum	Lead
Antimony	Magnesium
Ammonium	Manganese
Arsenic	Mercury (ous)
Barium	Mercury (ic)
Bismuth	Nickel
Cadmium	Potassium
Calcium	Silver
Cobalt	Sodium
Chromium	Strontium
Copper	Tin (ous)
Iron (ous)	Tin (ic)
Iron (ic)	Zinc

Your notes should have the form: —

Copper sulfate	No precipitate
Calcium chlorid	No precipitate
Silver nitrate	White precipitate

$$AgNO_3 + HCl = \underline{AgCl} + HNO_3.$$

The precipitate is indicated by underlining the formula. Which of the elements tested form insoluble chlorids? Which may be separated from the rest by the action of hydrochloric acid? These elements constitute the first group.

Experiment CXXV. To determine which of the common metals form sulfids which are insoluble in acidulated water. — Test each of the metals in the above list as follows: Add a few drops of hydrochloric acid to give the solution an acid reaction, then add a solution of hydrogen sulfid drop by drop, and heat. Which bases are precipitated? Which bases form light-colored precipitates? Which bases

form dark-colored precipitates? What sulfids are insoluble in acidulated water? These constitute the second group. What constituent of the hydrogen sulfid enters into these precipitates?

Experiment CXXVI. To determine which of the common bases form sulfids which are insoluble in free ammonium hydroxid (hydrogen sulfid is an acid, hence it is best to use one of its salts as the reagent).

1. Test each of the bases included in the above list as follows: —

2. Add ammonium hydroxid until the solution has an alkaline reaction, then add ammonium sulfid. Which bases are precipitated by ammonium hydroxid alone? which by ammonium hydroxid and ammonium sulfid? Of the latter bases, which is not precipitated when ammonium chlorid is present in excess?

It is more convenient to exclude from the third and fourth groups the substance not precipitated in the presence of ammonium chlorid. We therefore add an *excess* of this reagent to the solution under examination, thus throwing this substance, which would otherwise appear in the third group, into the fifth group. Which sulfids are insoluble in an alkaline menstrum? Which elements belong to the third group?

Experiment CXXVII. To determine which of the common bases form carbonates which are insoluble in an alkaline menstrum. — Test at least one substance containing each metal mentioned on page 229, as follows: Add ammonium hydrate until the solution has an alkaline reaction, then add ammonium carbonate. What bases are precipitated? What carbonates are insoluble in alkaline water? Which are soluble? What bases are precipitated by ammonium carbonate and not by ammonium sulfid? If the bases included in the first three groups had been removed from the solution, which of the remaining would be precipitated by ammonium carbonate? Of these, which is not precipitated when ammonium chlorid is present in excess? If you had a solution containing silver and calcium, how could you separate them? How could you separate lead, copper, and iron? Cadmium, barium, and potassium? How could you separate sodium, potassium, and ammonium from all the others tested? Make a list of the elements tested, dividing them into five groups.

Fill out the following table in your note-book, writing the symbols of the metals of each group in appropriate column : —

GROUPING OF THE METALS

<table>
<tr><td colspan="4">To solution containing any metal add HCl</td></tr>
<tr><td>PRECIPITATE
Group I</td><td colspan="3">FILTRATE ; add H_2S</td></tr>
<tr><td></td><td>PRECIPITATE
Group II</td><td colspan="2">FILTRATE ; add $NH_4HO + NH_4Cl + (NH_4)_2S$</td></tr>
<tr><td></td><td></td><td>PRECIPITATE
Group III</td><td>FILTRATE ; add
$NH_4HO + (NH_4)_2CO_3$</td></tr>
<tr><td></td><td></td><td></td><td>PRECIPITATE
Group IV</td><td>FILTRATE
Group V</td></tr>
</table>

ANALYSIS OF AN UNKNOWN SUBSTANCE

345. Preparing the Solution. — The scheme of analysis, based upon the facts brought out in the experiments just completed, is known as the *wet process* to distinguish it from the process based upon tests applied directly to the solid substance, which is known as the *dry process.* The wet process requires that the substance under examination be dissolved in some solvent before any reagents are added. This solution should be transparent and free from solid particles, and should be obtained by the complete solution of a portion of the substance, as this is the only way that one can be sure that all the substances in a mixture are tested. If the substance under examination is a solid, put a small amount of it in a test tube with 2 or 3 cc. of *distilled water;* if it does not dissolve, apply heat; if this fails, add a few drops of concentrated hydrochloric acid, and boil the substance a short time. If the substance is insoluble in

acidulated water, pour off the liquid and try *strong hydrochloric acid;* if this fails to dissolve it, add one-third as much *strong nitric acid* as you have of the hydrochloric (2). If the substance is insoluble in the aqua regia thus formed, it must be *fused* with sodium carbonate on platinum foil (3).

NOTES. — 1. If a white residue is obtained here that resembles silver or lead chlorid, treat a fresh portion of the substance with nitric acid.

2. If much strong hydrochloric acid has been used, or if any nitric acid has been added, it is necessary to evaporate to dryness before passing to group 2. (See note 1, article 352.)

3. Place a small quantity of the original substance on a piece of platinum foil or a piece of porcelain; cover it with 5 or 6 times its volume of sodium carbonate, and heat before the blowpipe until the effervescence has ceased and the mixture is fused to a thin liquid; this may require 10 or 15 minutes. Boil the fused mass with water; filter and wash any residue; dissolve a portion in dilute nitric acid, and test for group 1. Dissolve the remainder in dilute hydrochloric acid. Save a portion of the water solution for acid tests, and pour the remainder into the hydrochloric solution, and test for metals as usual.

346. As a precipitate is a solid, it may be collected on filter paper. The filtrate, as the filtered liquid is called, may contain more of the metal which was precipitated if the reagent was used sparingly, and as this may interfere with subsequent test, the student should always test the filtrate with a drop or two of the reagent which formed the precipitate. If a precipitate is again formed, pour the filtrate on the filter again, repeating the process until certain that all of the metal has been removed. Much unnecessary work may be saved if the student will remember that reagents lose their characteristic properties when they take part in a chemical change; therefore, we may be certain that enough of a reagent, having an odor or a color, has been added to entirely remove any metals which it can precipitate, when the liquid tested has acquired the

odor or the color of the reagent. It is hardly necessary to add that the above statement does not apply to those cases in which an *excess* of the reagent is required, either for the complete precipitation of the substance which is required in the solid state, or to prevent the precipitation of some substance which we wish to keep in solution. We are certain that enough hydrogen sulfid, ammonium sulfid, or ammonia has been added when the odor of the reagent can be detected in the liquid.

347. Washing Precipitates. — The success of the student in qualitative analysis will largely depend upon the attention which he pays to the directions given in the preceding paragraph, the care with which he washes his precipitates, and the purity of his reagents. The chief end to be attained by the precipitation of a substance is its separation from other substances; hence, precipitates must be washed until they are entirely free from the liquid in which they were formed. Precipitates are usually washed on the filter. After the filtrate has all passed through the filter paper add 1 or 2 cc. of water from the wash bottle; the jet should strike the filter paper near the upper edge, so that the precipitate may be carried down to the apex of the filter. When all of the wash water has passed through, repeat the process. Much time may be saved by washing precipitates with several small quantities of water rather than fewer large quantities.

It is not enough to *think* that the washing is sufficient; the student must *know*. Washing should be continued as long as the wash water gives a test for any substance known to be in filtrate; *e.g.* first group precipitates should be washed until the wash water does not redden blue litmus paper, showing absence of hydrochloric acid.

348. The Analysis. — Every analysis is begun by testing for group one, as directed in § 349, and passing to subsequent articles as directed. If it is known that only one substance is present, the filtrate remaining when the group precipitate is filtered out may be discarded.

THE FIRST GROUP

349. Precipitation. — (*a*) If the solution is alkaline or neutral, add nitric acid to distinct acid reaction (1).

(*b*) Add dilute hydrochloric acid, drop by drop, as long as a precipitate is formed (2), (3).

(*c*) Filter and treat the *precipitate* as directed in § 351.

(*d*) If metals, not in the first group, may be present, the *filtrate* must be treated as directed in § 352.

(*e*) If no precipitate is obtained, treat the solution as directed in § 352.

NOTES. — 1. The solution must have an acid reaction before the analysis is begun, as many members of the subsequent groups which are soluble in alkaline solution are precipitated when the solution is acidified, and would, therefore, mislead the student.

2. Avoid the excess of hydrochloric acid, and do not use the concentrated acid.

3. Dilute hydrochloric acid sometimes precipitates bismuth and antimony here, but the precipitate dissolves when more of the acid is added. If in doubt, test a separate portion of the original solution with a drop of concentrated hydrochloric acid; if no precipitate is formed, no first group element is present.

350. Separation of the First Group Metals.

Experiment CXXVIII. — Examine a filtered and washed precipitate of each first group metal to determine which chlorid is soluble in hot water and how each is affected by ammonium hydroxid. How could you determine which of the first group metals in an unknown solution containing one of them? If a solution contained silver and lead, how could you separate them?

These properties enable us to separate the first group metals, and to prove the presence or absence of either of them.

Experiment CXXIX. — 1. Pour about 1 cc. of a solution of each of the following nitrates into a test tube : (*a*) silver nitrate, (*b*) plumbic nitrate, (*c*) mercurous nitrate.

2. Precipitate as directed in § 349.

3. Follow the directions in § 351; endeavor to find a reason for each step.

351. Analysis of Group I

Wash the precipitate with cold water, using as little as possible; then treat with much hot water. Why? See notes (1) and (2).

<table>
<tr><td colspan="2">Residue = AgCl or HgCl or both
Add NH_4OH</td><td colspan="3" rowspan="2">Solution, $PbCl_2$
Confirm by testing Three Portions of the solution as follows :</td></tr>
<tr><td>Residue — black,
= NH_2Hg_2Cl
Hg present</td><td>Solution — AgCl
Add HNO_3 to acid reaction</td></tr>
<tr><td rowspan="2">Lead may occur here as white precipitate</td><td>Precipitate
= AgCl
Ag present</td><td>add H_2SO_4 to one part</td><td>add H_2S to another</td><td>add K_2CrO_4 to another</td></tr>
<tr><td colspan="3">Precipitate
Pb present</td></tr>
<tr><td colspan="2"></td><td>white
$PbSO_4$</td><td>black
PbS</td><td>yellow
$PbCrO_4$</td></tr>
</table>

Notes. — 1. Lead is not always precipitated in this group.

2. If the lead chlorid is not entirely dissolved by the hot water, the addition of the ammonium hydroxid changes what remains to a basic salt (white); this often passes through the filter, rendering the filtrate turbid. Nitric acid makes it clear again.

THE SECOND GROUP

352. Precipitation. — (*a*) Heat the filtrate from the first group (1), pass hydrogen sulfid through it as long as the precipitate increases (2), (3), or until the solution smells strongly of the gas.

(*b*) Heat to boiling, allow the precipitate to settle (4).

(*c*) Filter and wash the precipitate with hot water as long as the wash water reddens blue litmus (5).

(*d*) Dilute a portion of the filtrate with two or three times its volume of water and test again with hydrogen sulfid (6). If a precipitate is obtained, dilute the whole of the filtrate and treat with the group reagent until complete precipitation is secured. Pour on the filter paper containing the balance of the precipitate.

(*e*) If no precipitate is obtained, or if the *filtrate* may contain metals of subsequent groups, pass to § 357.

(*f*) Treat the group *precipitate* as directed in § 354.

NOTES. — 1. Hydrogen sulfid will not precipitate the second group metals from a solution containing much nitric acid or aqua regia. If either of these acids was used in dissolving the substance, evaporate to dryness in an evaporating dish, dissolve the residue in water containing a little hydrochloric acid, and pass the hydrogen sulfid through this solution.

2. If the solution contains a strong oxidizing agent, *e.g.* a nitrate, chlorate, chromate, or a ferric salt, a white precipitate of free sulfur is obtained.

3. Change of color from red to green, or from a colored to a colorless solution, does not indicate a second group substance. The former change is probably due to the presence of a chromate, the latter to a ferric salt. There are no white precipitates in the second group.

4. Some compounds of arsenic are precipitated very slowly from a cold solution, and rather slowly from a hot solution. Should a yellow precipitate form slowly, heat the solution nearly to boiling during the precipitation.

5. All traces of acid must be removed before proceeding to the separation of the metals of this group.

6. The second group metals must be entirely removed before proceeding to the next group. As the presence of too much hydrochloric acid sometimes prevents complete precipitation, it is best to dilute the filtrate before the final test.

353. The Sub-groups.

Experiment CXXX. — 1. Determine which of the eight sulfids precipitated in this group are soluble in yellow ammonium sulfid.

2. Filter each precipitate, wash, and pour the yellow ammonium sulfid on the paper. Notice whether any of the precipitate is dissolved. It is not always necessary to wait for it all to dissolve. The three metals which are soluble constitute the tin sub-group, the others are the copper sub-group.

354. The Separation into Sub-groups. — *a.* Make a hole in the bottom of the filter paper and wash the precipitate through it into a test tube, using as little water as possible.

b. Warm the precipitate in the test tube with yellow ammonium sulfid, and filter again.

c. The filtrate will contain the metals of the tin sub-group, and the precipitates those of the copper sub-group.

d. Treat the *filtrate* as directed in § 356, if a substance belonging to this group may be present.

e. Treat the *precipitate* as directed in § 355.

355. Separation of the Metals of the Copper Sub-group.

DIRECTIONS

PRECIPITATE (1), HgS, PbS, Bi_2S_3, CdS, CuS
Boil with HNO_3 (2). Replace evaporated acid

RESIDUE	SOLUTION $Pb(NO_3)_2$, $Bi(NO_3)_2$, $Cu(NO_3)_2$, $Cd(NO_3)_2$. Add H_2SO_4 (5)		
Dissolve in HCl and $KClO_3$ (4) Add $SnCl_2$ Precipitate $HgCl_2$ Hg present	PRECIP. = $PbSO_4$ Pb present	FILTRATE Bi, Cd, and Cu salts. Add NH_4OH (6)	
		PRECIP. = BiO_3H_3 Dissolve in HCl (7) pour into water Precip. (8) BiOCl Bi present	FILTRATE Cd and Cu. Add KCN and H_2S (9)
			PRECIP. CdS (10) Cd present / SOLUTION (11) KCN CuCN Cu present

NOTES. — 1. If the precipitate has been exposed to the air for some time, it should be washed with a few drops of yellow ammonium sulfid and then with water before treating with nitric acid. Wash until wash water is neutral.

2. Transfer the precipitate to an evaporating dish for this operation; boil for several minutes or until dissolved; filter and wash the residue, if any.

3. If too little nitric acid was used, other sulfids than that of mercury may occur here. The stannous chlorid test should therefore always be tried. Mercury sometimes occurs here as a yellow residue.

4. Use only a small crystal of potassium chlorate and boil until the vapor no longer bleaches litmus paper before adding the stannous chlorid.

5. To the filtrate from the mercuric sulfid add about 5 cc. of strong sulfuric acid and boil in an evaporating dish until white fumes appear (this proves that nitric acid has been expelled). When cool, dilute to ten volumes and transfer to a beaker; filter if turbid.

6. Add ammonium hydroxid to slight alkaline reaction. Then if a precipitate appears, a small quantity more to redissolve any copper or cadmium that may be precipitated; heat gently and filter.

7. Wash the precipitate, then pour a little strong hydrochloric acid on the filter; catch it in an evaporating dish and evaporate the solution until only a few drops remain; pour these into a beaker of water.

8. Failure to follow the directions in note 5 will cause a precipitate of lead to appear when ammonium hydroxid is added, hence, the confirmatory test should always be tried.

9. If the filtrate from the bismuth hydroxid is distinctly blue, we may conclude that copper is present and test for cadmium with potassium cyanide and hydrogen sulfid. If not blue, the following more sensitive test for copper should be applied. Acidify a small portion of the filtrate with acetic acid and add potassium ferrocyanid $K_4Fe(CN)_6$; a reddish brown precipitate indicates copper.

10. A yellow solution does not prove the presence of cadmium, but a yellow precipitate does.

11. Test this, or the original solution, with metallic iron; if copper is present, it will be deposited on clean surfaces.

356. Separation of the Tin Sub-group. — Add dilute hydrochloric acid to the ammonium sulfid solution to slight acid reaction; filter, dry the precipitate by suction, reject the filtrate, and treat the precipitate as directed below.

<table>
<tr><td colspan="4">Precipitate As_2S_5, Sb_2S_5, SnS_2. Add concentrated HCl (1)</td></tr>
<tr><td>Residue (2)
As_2S_5
Dissolve in
$HCl + KClO_3$ (3)
Add NH_4OH (4)
$NH_4Cl + MgCl_2$
Precip. (3)
$MgNH_4AsO_4$
As present</td><td colspan="3">Solution $SbCl_3$, $SnCl_4$
Place in hydrogen generator (6)
Collect gas in solution of $AgNO_3$ (7)</td></tr>
<tr><td></td><td>Generator (8)
Residue Sn
Dissolve in
strong HCl
Add $HgCl_2$
Precip. (9)
HgCl
white to gray
Sn present</td><td colspan="2">$AgNO_3$ Solution (10)
Precip. Ag, Sb
Digest with warm
HCl and dilute (11)
Divide
Add H_2S Precip. orange Sb_2S_5
Add H_2O Precip. white SbOCl
Sb present</td><td>Filtrate
H_2AsO_3
Add HCl (12)
Filter (13)
Add H_2S
Precip.
yellow
As_2O_5
As present</td></tr>
</table>

Notes. — 1. Heat *gently* in an evaporating dish as long as paper moistened with lead acetate is blackened by the vapors; add a little water and filter.

2. Wash the residue on the filter, then dissolve, using very little potassium chlorate.

3. Heat to expel the excess of chlorin.

4. Add ammonium hydroxid till alkaline, filter, if necessary, add half as much more ammonium hydroxid as you have of the solution, then add magnesia mixture, agitate, and set aside for 24 hours if no precipitate appears at first.

5. This precipitate is slightly soluble in water, and to a less extent in ammonium hydrate, hence traces of arsenic are likely to be lost unless the solution (3) is concentrated.

6. Place some strips of platinum, and a few small pieces of zinc known to be free of arsenic, in a test tube; add dilute hydrochloric acid and the solution to be tested; quickly insert stopper carrying a delivery tube, which shall conduct the gas through a solution of silver nitrate.

7. The gas evolved may be a poisonous one, and must not be inhaled. If tin was present, it will be found in the generator, which must be examined as directed in Note 8. If antimony was present, it will form a precipitate in the silver solution. Some arsenic may have been dissolved in the concentrated hydrochloric acid (1),

in which case it will be found here dissolved in the silver nitrate solution.

8. When the zinc has dissolved, pour the contents of the generator on a filter. Wash thoroughly, then dissolve the residue in strong hydrochloric acid.

9. The formation of a white or gray precipitate here proves the presence of tin, because the stannous chlorid which is formed when tin is present reduces the mercuric chlorid to mercurous chlorid, or to metallic mercury.

10. Filter and wash any precipitate in the silver solution.

11. Do not dilute to precipitation before dividing into two portions.

12. To remove silver, add hydrochloric acid, drop by drop, as long as a precipitate is formed, and filter.

13. A yellow precipitate formed by the hydrogen sulfid proves the presence of arsenic.

THE THIRD GROUP

357. Test for Phosphates. — If phosphates are present, the fourth group metals will be precipitated with those of the third group, and a more complicated method of separation must be used (1).

The Test. — Boil a small portion of the second group filtrate to expel hydrogen sulfid, acidify with nitric acid, and pour it into two volumes of ammonium molybdate $(NH_4)_2MoO_4$.

Agitate, and allow to stand for some minutes; if a *yellow precipitate appears*, phosphates are present, and the long process must be used. If phosphates are present treat the remainder of the second group *filtrate* as directed in § 362.

If phosphates are absent, treat the *filtrate* as directed in § 358.

NOTE. — The above test, and the table in § 362, are given for the convenience of those teachers who wish to include this case in their course. Doubtless few teachers will care to give pupils in secondary schools metals of the third or fourth groups in the presence of phosphates.

358. Separation into Sub-groups in the Absence of Phosphates. — (*a*) The filtrate from the second group, from which all second group substances have been removed, is now boiled until the vapor no longer blackens paper moistened with lead acetate (absence of hydrogen sulfid) (1).

(*b*) Add a few drops of nitric acid, and boil a short time (2).

(*c*) Add ammonium hydroxid to slight (3) alkaline reaction (4).

(*d*) Add decided excess of ammonium chlorid, say 15 or 20 cc. (5), (6).

(*e*) If a precipitate is obtained, a metal of the iron subgroup is present. Filter and wash any *precipitate*, and treat it as directed in § 359.

(*f*) Treat the *filtrate* as directed in § 360.

NOTES. — 1. If no first or second group substance is present, time will be saved by taking a fresh portion of the original solution, which need not be boiled; but this should not be done if the presence of a chromate was indicated when hydrogen sulfid was added (note 3, § 352) as the hydrogen sulfid reduces the chromium from its acid to its basic condition, and without this action the chromium would be detected only by the test for chromic acid.

2. If iron is present, it must be in the ferric state; boiling with nitric acid will transform it.

3. If too much ammonium hydroxid is added, aluminum will be dissolved.

4. If no precipitate is formed here, it proves the absence of interfering phosphates.

5. Ammonium hydroxid precipitates magnesium, but the precipitate dissolves in ammonium chlorid. If an opaque white precipitate is obtained, indicating magnesium, pour a few drops of the liquid containing it into a test tube, add 5 or 6 times as much ammonium chlorid. If the precipitate dissolves, add enough ammonium chlorid to the rest of the liquid to dissolve it.

6. The color of the precipitate indicates the metal present; aluminum is white and transparent; chromium is blue-green; iron is reddish brown.

359. Separation of the Iron Sub-group.

PRECIPITATE = $Fe_2(OH)_6$, $Cr_2(OH)_6$, $Al_2(OH)_6$
Boil in evaporating dish with NaOH (1)
Filter and wash any residue

PRECIPITATE = $Fe_2(OH)_6$, $Cr_2(OH)_6$ Divide in two parts		FILTRATE = $Na_6O_6Al_2$ Acidify with HCl, and add NH_4OH (5), white prec = Al present
I	II	
Dissolve in dilute HCl (2), (3) Fe present	Fuse with Na_2CO_3 and $KClO_3$ (4) yellow mass = Cr present	

NOTES. — 1. Add sodium hydroxid to alkaline reaction, then add 5 or 6 cc. more, and boil several minutes.

2. Dilute with water. To half of the solution add a few drops of potassium ferrocyanid, $K_4Fe(CN)_6$. A blue precipitate indicates iron. To the other half of the solution add potassium sulfocyanid, KCNS; a blood-red color indicates iron.

3. If iron is found, determine whether it is in the ferrous or ferric condition by testing portions of the *original solution* with potassium ferricyanid and with potassium sulfocyanid.

	FERROUS	FERRIC
Potassium sulfocyanid	no prec.	red solution
Potassium ferricyanid	blue prec. (dark)	green solution sometimes brown

4. If chromium is present, a yellow mass of sodium chromate is obtained. To confirm, boil the fused mass in water, acidify with acetic acid, boil again, and add lead acetate; a yellow precipitate confirms the presence of chromium.

5. Add hydrochloric acid to acid reaction, then ammonium hydrate until alkaline, heat gently, and if no precipitate appears at once, set aside for half an hour. A flocculent white precipitate indicates aluminum.

360. Precipitation of the Cobalt Sub-group. — (*a*) To the filtrate from *f*, § 358, add colorless ammonium sulfid, filter and wash the precipitate (1). Add a little ammonium sulfid to the wash water.

(*b*) The *filtrate* must be tested for the metals of groups 4 and 5. Pass to § 364.

(*c*) Treat the *precipitate* as directed in § 361.

NOTE. — The precipitate formed by cobalt and nickel is black, that of manganese is flesh color, but turns brown on standing, and that of zinc is white.

361. Separation of the Cobalt Sub-group.

PRECIPITATE = CoS, NiS, MnS, ZnS
Dissolve on the filter with cold dilute HCl (1)
Receive the filtrate in an evaporating dish

RESIDUE — CoS, NiS (on filter paper) (2) Wash and dissolve in aqua regia (3) Add KCN (conc.)	SOLUTION — $ZnCl_2$, $MnCl_2$ Add decided excess of NaOH, digest without warming Filter	
PRECIPITATE (8)	PREC. $Mn(OH)_2$ (5) Fuse with KNO_3, and Na_2CO_3 Green mass (6) Mn present	SOL. Na_2ZnO_2 Add $(NH_4)_2S$ Prec. (7) Zn present
yellowish green insoluble in HCl Ni present / brownish white soluble in HCl Co present		
Test by (4)		

NOTES. — 1. Cobalt and nickel are often partially dissolved here, particularly if the acid is hot; in such case they will be found with the manganese precipitate.

2. If the hydrogen sulfid is not completely removed, zinc sulfid may be precipitated with the cobalt and nickel.

3. If the residue is not abundant, incinerate the filter and dissolve the residue as directed. Boil the solution as long as the vapor bleaches

litmus paper before adding the concentrated solution of potassium cyanid.

4. *The Borax Bead Test.* — Heat a piece of platinum wire, the end of which is bent so as to form a small loop, dip it in powdered borax while hot and hold it in the flame again; when the borax has melted and formed a transparent bead place some of the precipitate on it and heat again; cobalt forms a blue bead, nickel in the oxidizing flame forms a red bead while hot, becoming colorless when cool.

5. This precipitate must be tested for cobalt and nickel by the borax bead (4) or with aqua regia and potassium cyanid, as in the table.

6. Fuse on platinum foil or in a porcelain crucible, using six parts of the flux to one of the precipitate, continue heat until a thin liquid is obtained; a *green* mass indicates manganese.

7. To distinguish sulfur (from the group sulfids). Add hydrochloric acid. Sulfur does not dissolve; the sodium zincate does.

8. If both cobalt and nickel may be present, filter and wash this precipitate and treat it with hydrochloric acid; an insoluble residue indicates nickel. Confirm by the borax bead.

362. Precipitation of the Third Group in the Presence of Phosphates. — (*a*) To the second group filtrate, from which all second group substances have been removed and all hydrogen sulfid has been expelled, add ammonium hydroxid to slight alkaline reaction, then add decided excess of ammonium chlorid, and then ammonium sulfid as long as a precipitate is formed.

(*b*) Heat to boiling and shake until the precipitate subsides quickly.

(*c*) Filter and wash at once with water to which a little ammonium sulfid has been added.

(*d*) Test the *filtrate* for the fourth* and fifth group metals. Pass to § 364.

(*e*) Treat the *precipitate* as directed in § 363.

* This is necessary even though phosphates be present, because there may not be enough of the phosphates to cause the precipitation of all of the fourth group metals present.

363. Separation of the Third Group Metals in the Presence of Phosphates.

PRECIPITATE AlO_3H_3, CrO_3H_3, CoS, NiS, FeS, MnS, ZnS, $Ba_3(PO_4)_2$, $Sr_3(PO_4)_2$, $Ca_3(PO_4)_2$, $MgNH_4PO_4$
Treat with dilute HCl (1)

RESIDUE	SOLUTION $AlCl_3$, $CrCl_3$, $FeCl_2$, $MnCl_2$, $ZnCl_2$. $BaCl_2$, $SrCl_2$, $CaCl_2$, $MgCl_2$ Divide in three parts			
CoS, NiS Test for Co and Ni, as in § 361	I Add H_2SO_4 and alcohol		II Boil with HNO_3 (5) and add $K_4Fe(CN)_6$ precipitate (6) Fe present	III Treated as directed below
	PRECIPITATE $BaSO_4$ $CaSO_4$ $SrSO_4$ (3) (4)	FILTRATE Reject		

PART III

Boil with HNO_3, add Fe_2Cl_6 and $BaCO_3$ (7)

PRECIPITATE FeO_3H_3, AlO_3H_3, CrO_3H_3 $FePO_4$ ($BaCO_3$) Dissolve in HCl and add H_2SO_4 (8)		FILTRATE Add NH_4OH and $(NH)_2S$			
		PRECIPITATE MnS, ZnS. Dissolve in HCl and add NaOH (14)		FILTRATE Add $(NH_4)_2CO_3$ and $(NH_4)_2C_2O_4$	
PRECIP. $BaSO_4$ Reject	FILTRATE (9) Add NaOH and boil			PRECIP. Ba, etc. reject	FILTRATE (16) add Na_2HPO_4 (17) Prec. Mg pres.
	PREC. FeO_3H_3 CrO_3H_3 (10) Cr pres.	FILTRATE Add HCl and NH_4OH (12) Al pres.	PREC. MnO_2H_2 Fuse (15) Mn pres.	FILT. add H_2S Prec. Zn pres.	

NOTES. — 1. Boil the solution until hydrogen sulfid is entirely expelled.

2. Evaporate the first portion to dryness, add a little dilute sul-

furic acid and twice as much alcohol; set aside for a few minutes, filter and wash with a little alcohol.

3. Fuse on platinum foil with five parts of sodium carbonate. Boil with water, filter, and wash the precipitate. Dissolve in nitric acid and treat as directed in § 364.

4. This solution may be added to filtrate from the third group if the filtrate contains fourth group metals.

5. Boil the remaining portions in an evaporating dish with a little nitric acid, pour a little of it into a test tube, dilute and add two or three drops of potassium ferrocyanid; a blue precipitate indicates iron.

6. If iron is found, test the original solution as directed in note 3, § 359.

7. To the third portion in the evaporating dish (which has already been boiled in nitric acid) add ferric chlorid until a drop of the solution on a piece of glass gives a yellow precipitate with ammonium hydroxid. Evaporate nearly to dryness to expel acid, then add sodium carbonate as long as the precipitate formed is redissolved by shaking. Pour into a flask, dilute to 200 cc., cool, and add barium carbonate (not too much) agitate frequently for half an hour. Filter and wash the precipitate.

8. Dissolve in dilute hydrochloric acid. Boil and add dilute sulfuric acid; after a few minutes, filter; throw the precipitate away.

9. Add sodium hydroxid to strong alkaline reaction. Boil a few minutes and filter.

10. Fuse the precipitate with sodium carbonate and potassium chlorate; a yellow mass indicates chromium. Confirm by (4), § 359.

11. Acidify the filtrate with hydrochloric acid, add ammonium hydroxid till slightly alkaline; heat and set aside for half an hour if no precipitate appears at first. A precipitate indicates aluminum.

12. Add a few drops of hydrochloric acid, and boil to expel carbon dioxid. Then add ammonium hydroxid till alkaline, and add a small quantity of ammonium sulfid; if a precipitate appears, filter and wash.

13. The sodium hydroxid is added until the solution is alkaline.

14. Test the precipitate for manganese as directed in note 6, § 361.

15. Concentrate the filtrate, add one-third its volume of ammonium hydroxid and a little disodic hydric phosphate.

16. Stir with a glass rod, set aside for 24 hours if no precipitate appears at once.

THE FOURTH GROUP

364. Precipitation. — (*a*) To the filtrate from the third group (1) containing ammonium chlorid, add ammonium hydroxid and carbonate; heat gently for some minutes.

(*b*) Filter out any precipitate, reserving the *filtrate* to be tested for the fifth group metals, § 366.

(*c*) The *precipitate* is composed of fourth group metals, and is to be treated as directed below, § 365.

365. Separation of the Fourth Group Metals.

PRECIPITATE. $BaCO_3$, $SrCO_3$, $CaCO_3$
Wash and dissolve in dilute acetic acid

SOLUTION. $Ba(C_2H_3O_2)_2$, $Sr(C_2H_3O_2)_2$, $Ca(C_2H_3O_2)_2$
To a small portion add K_2CrO_4; if a precipitate is formed, add to the whole and filter (2)

PRECIPITATE	SOLUTION. $Sr(C_2H_3O_2)_2$, $Ca(C_3H_3O_2)_2$		
$BaCrO_4$, yellow, soluble in HCl (3) Ba present	Add NH_4OH and $(NH_4)_2CO_3$, filter and wash the precipitate. Dissolve it in HCl Evaporate to dryness; add H_2O (4) Divide into two portions		
	I Add $CaSO_4$ and boil (5) Prec. (6), white Sr present	II Add K_2SO_4 (7)	
		PRECIPITATE Reject	FILTRATE Add NH_4OH and $(NH_4)_2C_2O_4$ Precipitate (8) Ca present

NOTES. — 1. The filtrate from the ammonium sulfid precipitate should be colorless or light yellow. If brown or black, nickel is probably present; remove it by adding acetic acid to acid reaction, boiling and filtering; if pink, chromium is indicated; remove it by boiling and filtering; a green color is due to traces of iron which settle to the bottom on standing.

If no precipitate is obtained in the preceding groups, the fourth group precipitate may be obtained by adding ammonium hydrate to the original solution, to alkaline reaction, then adding ammonium chlorid and carbonate.

2. Before adding the potassium chromate, dilute the solution with 30 cc. of water, heat to boiling, and add the chromate gradually.

3. Precipitate again with sulfuric acid. A white precipitate insoluble in all acids confirms the presence of barium.

4. This solution should be neutral to litmus.

5. If a precipitate does not appear at once, set aside for ten minutes.

6. Test by flame. The flame of strontium is crimson, that of barium yellowish green, and that of calcium yellowish red.

7. Potassium sulfate must be added as long as a precipitate is produced in order to remove strontium, which would interfere with the test for calcium. Filter and reject any precipitate.

8. This precipitate is insoluble in acetic acid, but dissolves in hydrochloric acid.

THE FIFTH GROUP

366. This group includes all the metals not precipitated in the preceding groups. Divide the filtrate from the fourth group into two portions, and test as directed below.

1. To the first portion, add a little ammonium hydroxid, then enough ammonium chlorid to dissolve any precipitate that appears; then add sodium phosphate, Na_2HPO_4; a white precipitate indicates magnesium (1) (2).

2. Test the second portion by flame (3) (4). Violet, not obscured by blue glass, indicates potassium (5). Yellow, obscured by blue glass, indicates sodium.

367. The Ammonia Test. — The original solution or solid substance should be tested for ammonium salts as follows.

Place a small amount of the substance in a beaker, add solid calcium hydroxid, moisten with a little water. Cover the beaker with a glass plate, to the under side of which a piece of moist red litmus is attached. Heat gently. If ammonium is present, the vapor will turn litmus paper blue.

Note the odor. (Care.) Hold the stopper of the hydrochloric acid bottle over the beaker; a white cloud will be formed if ammonium is present. Confirm by testing with Nessler's reagent, § 82.

Notes. — 1. If calcium was found in the fourth group, traces may appear here; to prevent interference with subsequent tests add ammonium oxalate $(NH_4)_2C_2O_4$ to the fourth group filtrate and filter. If barium was found, remove it by precipitating with ammonium sulfate and filtering. Reject the filtrate. Reject the precipitate in each case, and concentrate the filtrate until crystals appear, then test as directed.

2. The magnesium precipitate is crystalline. If flocculent, it probably consists of aluminum dissolved because too much ammonium hydroxid was used in precipitating the third group metals.

3. If magnesium is abundant, it will interfere with the flame tests; to remove it add barium hydroxid, filter, add dilute sulfuric acid to the filtrate, and filter again; this filtrate will contain no magnesium.

4. Evaporate the solution to dryness; introduce a little of the residue into the flame of a Bunsen burner.

5. Ignite a small portion of the residue on platinum foil to faint redness; dissolve in the least possible quantity of water, add a few drops of hydrochloric acid, and the same amount of platinum chlorid, stir, and set aside a short time; a precipitate indicates potassium.

ACID TESTS

368. The Removal of Bases. — Certain bases interfere with the acid tests; in cases in which the acid tests, §§ 369–373, are indeterminate the following directions should be followed.

(*a*) *The Substance is Soluble in Water.* 1. If the substance is in the fourth or fifth group, the original solution may be used for acid tests.

2. If the substance contains metals of the first, second, or third group, add sodium carbonate as long as a precipitate continues to form; filter and test the filtrate for acids.

(*b*) *The Substance is Insoluble in Water.* 3. If the substance contains metals of the third, fourth, or fifth group, boil some of the solid with a strong solution of sodium carbonate for ten minutes, replacing the water which evaporates. Filter; acidify one portion with sulfuric acid, boil to expel carbon dioxid, and test for nitric acid; boil as before and test as in §§ 370, 371.

4. If a metal precipitated by hydrogen sulfid is present, suspend the substance in water, and pass hydrogen sulfid through the solution as long as a precipitate forms. Boil a short time; filter, expel hydrogen sulfid, and test the filtrate for acids.

369. Suggestions. — 1. To the solid under examination or a concentrated solution, in a small test tube, add a few drops of strong sulfuric acid.

2. Sudden effervescence indicates a carbonate.
3. Slight effervescence indicates an oxalate.
4. Odor of hydrogen sulfid indicates a sulfid.
5. Odor of vinegar indicates an acetate.
6. Odor of burning matches indicates a sulfite.
7. Violet vapor indicates an iodid.
8. Yellow vapor indicates a bromid.
9. White cloud with ammonium hydroxid indicates a chlorid.

370. For Sulfuric Acid. — To a portion of the original solution add barium chlorid. A white precipitate insoluble in dilute hydrochloric acid proves the presence of a sulfate.

371. For Hydrochloric Acid. — To the original solution add a few drops of silver nitrate solution; a white precipitate insoluble in nitric acid, but soluble in ammonium hydroxid, indicates a chlorid.

372. For Nitric Acid. — Pour a cubic centimetre of strong sulfuric acid into a test tube, add an equal volume of the solution to be tested; when cool pour a concentrated solution of ferrous sulfate carefully down the sides of the tube. A brown ring where the two liquids meet indicates nitric acid.

373. For Carbonic Acid. — Treat a concentrated solution of the original substance with hydrochloric acid; if effervescence occurs, hold a drop of barium hydrate on the end of a glass rod just above the surface of the liquid; if it becomes turbid, carbonic acid is indicated.

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